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A study of the dissolution of titanium in acids with ammonium fluoride added

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The undersigned, appointed by the Dean of the Graduate Faculty, have examined a thesis entitled A Study of the Dissolution of Titanium in Acids with Ammonium Fluoride Added.

presented by Charles Burroughs Gill

a candidate for the degree of Ph. D. in Metallurgical Engineering

and hereby certify that in their opinion it is worthy of acceptance.

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A STUDY OF THE DISSOLUTION OF TITANIUM IN ACIDS WITH AMMONIUM FLUORIDE ADDED

by

Charles Burroughs Gill

Submitted in Partial Fulfillment of

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CHAPTER 1

Introduction

Titanium can no longer be considered a rare metal, even though the modern era of its production came into being only a few years ago. The first discovery of titanium was in 1791 by an English clergyman, the Reverend William Gregor, and the name titanium became universally adopted when so called by a German mineralogist, Martin Klaproth, who rediscovered titanium three years later. Not until 1887 was the relatively pure, 75 percent, metal prepared by L. F. Nilson and O. Pettersson, whose experiments were repeated in 1910 by M. A. Hunter. Hunter is given credit for producing the first metallic titanium pure enough to be malleable while cold. However, since that time progress was somewhat more rapid, and there are several accounts in the German literature of relatively pure ductile titanium being prepared as far back as 1925.

The chief reasons for the enthusiasm being shown for titanium, are its fortunate combination of desirous physical and chemical properties, and its relative abundance. Ductile titanium and its alloys possess a good combination of strength, lightness, high proportional limit, high modulus of elasticity, high electrical resistivity, high melting point, low coefficient of thermal expansion, low thermal conductivity, and good corrosion resistance. F. W. Clarke in his survey of the relative abundance of elements for the U. S. Geological Survey, placed titanium as being ninth, 0.529 percent, in abundance in

elements of the earth's crust. That is, twenty times as abundant as all the copper, nickel, zinc, tin, lead and molybdenum combined. Also, titanium is found concentrated in sufficiently large deposits for economical mining and recovery.

The strength-weight ratio of some of the alloys of titanium is high, well above that of any other structural material. While elemental titanium ranks only after aluminum, iron and magnesium as a structural metal. Then too, the strength is retained well at moderately elevated temperatures where aluminum and magnesium have lost much of their strength. Titanium may also be hot forged, machined about as easily as stainless steel, and spot or arc welded in an inert atmosphere.

The corrosion resistance of titanium is good, and compares favourably with stainless steel. It is not attacked by the atmosphere, and has excellent resistance to sea water, humid and saline atmospheres, and nitric acid. While at present not enough conclusive evidence has been gathered to place the corrosion resistance exactly, it seems at least to be on a level with chromium and nickel.

While several papers have been published within the past year or two on the corrosion of pure titanium, these papers dwell on corrosion rates in various acids of different concentrations, and are not too much concerned with the mechanism of the corrosion process. In view of this, it was thought worthwhile to continue the study of titanium corrosion a step further, and to determine if an addition agent would have any effect on the corrosion rate, when added to an

acid in which pure titanium was relatively unaffected.

As it has been found that pure titanium is most rapidly attacked by hydrofluoric acid [1] and attacked very slowly by sulphuric,

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1) Straumanis, M. E., and Chen, P. C., The Corrosion of Titanium in Acids, Corrosion, 7, No. 7, 229-237, (1951)

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nitric, and hydrochloric acids, it was decided to add ammonium fluoride to these slower attacking acids. This would serve the purpose of introducing a fluorine ion in controlled, limited amounts, in sufficient quantity to remove the corrosion resistant surface layer of the titanium, and then give the ordinarily ineffective acids an opportunity to attack the titanium surface now exposed. This would show if there is a skin effect on the surface of the titanium, the skin being highly corrosion resistant. At the same time other investigations would be carried out to try and determine the mechanism by which the titanium is attacked.

CHAPTER II

Review of The Literature

References in the literature about the corrosion of titanium are rather few, and until the past few years consisted mainly of merely qualitative statements. This of course is to be expected, as it is only within a comparatively short time that pure titanium has been produced in sufficient quantity to warrant any extensive investigation of its properties. Then too, as the purity of the titanium produced by older experimenters is much less than that of the modern product, their findings are not too reliable as applied to present day commercially pure titanium.

(i) Literature concerning the dissolution of impure titanium.

A comprehensive summary of the work of early investigators from 1863 to 1910 is given by J. W. Mellor [1], and this work can be considered to cover the period when so called pure titanium was of the order of 75 percent, as compared with over 99 percent titanium now available.

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1) Mellor, J. W., A Comprehensive Treatise on Inorganic and Theoretical Chemistry, London, Longman Green and Co., 7, 19, (1927)

(1) Hydrofluoric Acid: V. Merz, L. Weiss and H. Kaiser [1] found titanium was readily dissolved by hydrofluoric acid, which according to O. Ruff [2] gave a solution of tetrafluoride with anhydrous hydrogen fluoride gas at 700° C.

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2) Ruff, O., Ipsen, R., Ueber das Titanfluorid. Ber. d. deutechen Chem. Ges., 36, 1777, (1903)

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(2) Sulphuric Acid: V. Merz, L. Weiss, H. Kaiser and H. Moissan [1] found cold dilute sulphuric acid dissolved titanium readily, with the evolution of hydrogen, but that heat is necessary for a continuous reaction. Hot concentrated sulphuric acid also oxidized titanium to form SO_2.

(3) Hydrochloric Acid: H. Moissan, L. Weiss, and H. Kaiser[1] found boiling hydrochloric acid attacks titanium slowly, with hydrogen evolved and a violet coloured solution formed.

(4) Fluorine: O. Ruff and I. Ipsen [2] found fluorine reacts with hot titanium, forming the tetrafluoride.

(5) Nitric Acid: V. Merz, L. Weiss and H. Kaiser [1] found that titanium is slowly attacked by cold, dilute nitric acid, and more quickly by hot acid. R. Weber [1], using HNO_3 of sp. gr. 1.25, found much titanic oxide was formed which did not dissolve.

(6) Aqua Regia: V. Merz, L. Weiss and H. Kaiser [1] found

titanium dissolved much faster in aqua regis than nitric acid alone, but the coating of titanic oxide formed soon stops the reaction.

(7) Acetic Acid: V. Merz [1] found titanium is attacked very slowly by acetic acid.

(ii) Literature concerning the dissolution of relatively pure titanium.

The majority of the papers in recent literature are concerned primarily with the rates of dissolution of titanium in various solutions and only two papers by M. E. Straumanis and P. C. Chen [3][4] go

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3) Straumanis, M. E., and Chen, P. C., The Mechanism and Rate of Dissolution of Titanium in Hydrofluoric Acid, Journal of The Electrochemical Society, 98, No. 7, 234-240, (1951)

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4) Straumanis, M. E., and Chen, P. C., The Difference Effect on Titanium Dissolving in Hydrofluoric Acid, Journal of The Electrochemical Society, 98, No. 9, 351-355, (1951)

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into the mechanics of dissolution. Their investigations showed that titanium is rapidly dissolved by hydrofluoric acid forming the trifluoride instead of the tetrafluoride which earlier experimenters claimed resulted. They also showed dissolution might be an electrochemical process, the velocity of which is determined by the activity of local cells. The cathodes of these cells being the impurities in the titanium. This was substantiated by their work on difference effect.

W. J. Kroll [5] states pure titanium behaves very much like 18-8 stainless steel, being unattacked by cold or boiling water, and reacting with steam at 800° C. Also it is attacked by cold, dilute

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5) Kroll, W. J., Titanium, Corrosion Handbook, New York, John Wiley and Sons, Inc., 329, (1948)

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hydrochloric, sulphuric and hydrofluoric acid, while nitric acid is not reactive, and passivates the metal so that it is more resistant to hydrochloric and sulphuric acids. Mixtures of hydrofluoric and nitric acids are more corrosive than hydrofluoric alone, and the metal will react with fluorine at elevated temperatures.

There are several articles dealing with the dissolution rates of titanium. R. S. Dean [6] and his associates state that 5 percent

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6) Dean, R. S., Long, J. R., Wartman, F. S., and Anderson, E. L., Preparation and Properties of Ductile Titanium, Metals Technology, 13, No. 2, 12-13, (1946)

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sulphuric acid causes a loss of weight of 0.4 milligrams per square decimeter per day, while a 5 percent solutions of hydrochloric acid, ammonium hydroxide, sodium hydroxide and acetic acid do not cause a loss of weight in excess of 0.05 milligrams per square decimeter per day.

These corrosion rates are in accord with the finding of

E. A. Gee [7] and his associates, who also state that titanium is

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7) Gee, E. A., Long, J. R., and Waggaman, W. H., Metallic Titanium is Light, Strong, Durable, and Corrosion Resistant, Materials and Methods, 27, 75-78, (1948)

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soluble in higher concentrations of H Cl, and is readily attacked by sulphuric acid.

E. A. Gee [8] is also responsible for further corrosion tests with titanium, using sulphuric, hydrochloric and nitric acids with aeration for 144 hours. They found annealed titanium to be rapidly

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8) Gee, E. A., Golden, L. B., and Lusby, W. E. Jr., Titanium and Zirconium Corrosion Studies Common Mineral Acids, Industrial and Engineering Chemistry, 41, 8, 1668-1673, (1949)

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attacked by sulphuric acid in all concentrations above 5 percent, with the maximum corrosion rate at 40 percent acid, and the minimum at 65 percent acid. Cold rolled titanium dissolved at approximately the same rate as the annealed, except the rate exceeded that of the annealed metal in 10, 25 and 40 percent acid. The maximum rate at 35° C for annealed titanium was 1069 milligrams per square decimeter per day, and for cold rolled, 1331 milligrams per square decimeter per day. With hydrochloric acid, annealed titanium was resistant to corrosion below 5 percent acid at 35° C, 3 percent acid at 60° C, and 1 percent acid at 100° C. Nitric acid in 5 and 10 percent solutions

showed only slight attack at 35 and 100° C, and the metal was also resistant to boiling glacial acetic acid, 10 percent sodium hydroxide, and various food juices.

H. G. Fontana 9) reported cumulative corrosion rates for 168 hours of 6.265, and 240 mils per year in 3.65, and 93 percent sulphuric acid; of 0.2, 0.6 and 1 mils per year in 0.5, 0.75 and 1.0 percent

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9) Fontana, H. G., Corrosion, Industrial and Engineering Chemistry, 40, 10, 99A-100A, (1948)

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hydrochloric acid; of 25 mils per year in 3 percent sodium chloride solution; and a negligible rate for 10 percent nitric acid and 10 percent acetic acid.

Quite an extensive study has been made by G. E. Hutchinson 10) and P. H. Permar into the reagents which react with titanium, and

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10) Hutchinson, G. E., and Permar, P. H., Corrosion Resistance of Commercially Pure Titanium, Corrosion, 5, 10, 319-325, (1949)

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using the arbitrary value of rates in excess of 0.005 inches per year being reactive, lists; 50 percent boiling formic acid, greater than 5 percent hydrochloric acid at 25° C and 1 percent boiling, all aqueous solutions of hydrofluoric acid, 65 percent boiling nitric acid, 10 percent phosphoric acid at 80° C and 85 percent at 25° C, and 5 percent and greater sulphuric acid at 25° C, with 1 percent and greater at 80° C.

Using this same arbitrary value of 0.005 inches per year, the work of D. F. Taylor [11] would give as reactive, 18 percent and concentrated hydrochloric acid at 19-26° C, concentrated sulphuric acid

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11) Taylor, D. F., Acid Corrosion Resistance of Tantalum, Columbium, Zirconium and Titanium, Industrial and Engineering Chemistry, 42, 4, 639, (1950)

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at 19-26 and 145° C, and 85% phosphoric acid at 19-26° C.

The corrosion of titanium in sulphuric, hydrochloric, hydrobromic and hydriodic acids was investigated by M. E. Straumanis [12] and P. C. Chen, who showed that dissolution in these acids is similar

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12) Straumanis, M. E., Chen, P. C., The Corrosion of Titanium in Acids, Corrosion, 7, 7, 229-237, (1951)

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to that in hydrofluoric acid, forming the trifluoride. At 25° C the rate of dissolution of titanium in sulphuric and hydrochloric acids below 2N is very low, and is still lower in hydrobromic acids of all concentrations. Hydriodic acid is unreactive to the slightest degree. It was also shown the rate of dissolution was affected by impurities, and the formation of protective layers which could be removed by the addition of small amounts of ammonium fluoride. Potential measurements of titanium were made in sulphuric and hydrochloric acids, and showed that the potential became more anodic with time, and with increasing concentrations of the acids.

Some studies were made by E. D. Botts [13] and F. C. Krauskopf on the potential measurements of titanium, and they found titanium, in an ordinary cell, to be less active than hydrogen, and the single

13) Botts, E. D., and Krauskopf, F. C., Some Electrochemical Studies of Titanium, Journal of Physical Chemistry, 31[2], 1404-19, (1923)

potential of titanium greatly increased when a small amount of hydrofluoric acid is present. They also note that HCl and H_2SO_4 added to their respective salt solutions cause a decrease in the single potential of titanium, and alkali salts a slight increase. Titanium introduced into solutions of various fluorides produced only an evolution of gas from the titanium.

This present research problem was to enlarge upon, and more thoroughly investigate the effect of ammonium fluoride added to various acids, to discern how such additions concerned the corrosion of titanium as to rate of dissolution, and the nature and mechanism of this dissolution. None of this has been duplicated before except the mention by M. E. Straumanis [12] that the additions of ammonium fluoride will remove the protective layers on titanium and permit attack by otherwise slowly or non-reacting reagents.

CHAPTER III

Experimental Methods and Materials

PART I

Preliminary Qualitative Tests

A preliminary survey was conducted to see how titanium would react in various acids before and after the addition of ammonium and sodium fluoride. The titanium samples were polished, cold rolled sheet from the Remington Arms Company, and had a nominal purity of over 99 percent. The tests were carried out in test tubes at room temperature.

The results of these tests are as follows:

2N sulphuric acid

The titanium showed no attack when left in the acid alone, but when a small amount of ammonium fluoride was added the titanium was violently attacked as soon as the NH_4F went into solution. The titanium sample turned dull and lustreless as dissolution proceeded. The reaction gradually slowed down, but could be reactivated by new additions of small amounts of ammonium fluoride. The solution after the reaction was a dark, reddish brown colour, which on the addition of 0.05N potassium permangante solution, changed to a colourless liquid. As trivalent titanium solutions are coloured, and tetravalent colourless,

this seems to indicate the trivalent state was present, and oxidized to tetravalent by the $KMnO_4$ added.

4N sulphuric acid

Sodium fluoride instead of ammonium fluoride was used in this test, and there was no reaction with the titanium sample until the sodium fluoride was added, whereupon a vigorous reaction started immediately. The solution was coloured after the reaction finished, indicating the trivalent state, and the titanium sample had turned dark and dull. A blue grey precipitate collected around the titanium.

Dilute (4-1) nitric acid

There was no apparent reaction until ammonium fluoride was added, then a reaction began immediately with its vigour in direct proportion to the amount of NH_4F added. Several tests were made using varying amounts of ammonium fluoride as the initial addition, and that test which had a considerable amount of ammonium fluoride added dissolved the titanium completely leaving a white, fluffy precipitate. After the reaction gradually slowed down and stopped, in the tests where lesser amounts of NH_4F had been added initially, there was a white precipitate in each, in amounts proportional to the ammonium fluoride added, the solutions were colourless indicating the tetravalent state, and the titanium samples were not dissolved and were still bright and shiny. The white precipitate formed was very likely titanic oxide.

Concentrated nitric acid

In contrast to the dilute nitric acid, there was no reaction whatsoever, or else only sporadic reaction, unless a considerable amount of ammonium fluoride was added. In this case the reaction was steady and sustained. The titanium turned dark, and the solution coloured. After the reaction there was a fluffy, white precipitate around the dark titanium, and on standing the coloured trivalent solution oxidized to the colourless tetravalent state.

2N hydrochloric acid

There was no apparent reaction when the titanium sample was placed in the acid, but an immediate reaction was obtained when ammonium fluoride was added. The titanium turned dull and dark. The reaction very gradually slowed down and stopped, but could be started again by adding more ammonium fluoride. After the reaction the solution was a dark, reddish brown colour, which on further standing turned colourless, so was likely oxidized by standing exposed to air to the tetravalent state.

12 percent perchloric acid

There was no reaction whatsoever until the ammonium fluoride was added, whereupon an immediate reaction began, with the titanium sample losing its polish and turning a dull, dark grey colour, as previously observed. After standing in air the solution turned colourless from a dark green, indicating it was probably oxidized from the coloured

trivalent state to the colourless tetravalent. When this state was reached more ammonium fluoride was added but there was no reaction. Then fresh 12 percent $HClO_4$ was also added, and the reaction began again slowly, with the solution changing from colourless to light green. This phenomena was possibly due to all the perchloric acid originally added having been exhausted.

50 percent acetic acid

This acid showed no reaction until ammonium fluoride was added, after which there was a good reaction. However, the reaction slowed appreciably after a few hours and this may have been due to only the hydrofluoric acid available attacking the titanium, so that after the hydrofluoric acid formed from the ammonium fluoride was exhausted the reaction stopped, and the acetic acid alone did not react with the titanium.

The solutions turned colourless when the reaction was finished, and pink on the addition of a few drops of 0.05N potassium permanganate. Indicating the solution was oxidized to the tetravalent state. Upon the addition of a few drops of 4N sulphuric acid the reaction began again; this was probably due to the sulphuric acid attacking the titanium.

50 percent formic acid

Again there was no reaction until the ammonium fluoride was added, whereupon a steady, strong reaction began with the titanium sample

turning dark. The solution turned greenish, but was colourless at the end of the reaction, indicating the tetravalent state, though on the addition of more ammonium fluoride the reaction began again and the solution turned green, indicating the trivalent state.

100 percent trifluoracetic acid

The titanium remained bright and shiny until the ammonium fluoride was added. After which the solution turned somewhat murky, the titanium turned dark, and an extremely weak reaction took place for a short time. The addition of more ammonium fluoride repeated the short, weak reaction.

75 percent trifluoracetic acid

In this case there was no reaction before the ammonium fluoride was added, and an immediate, strong reaction, which quickly slowed, and steadied, after the addition. The solution turned green, indicating the trivalent state, then on standing turned colourless, the tetravalent state. A white precipitate collected around the darkened titanium, and the additions of further ammonium fluoride started a moderately strong reaction which soon slowed drastically.

50 percent trifluoracetic acid

There was no reaction before the ammonium fluoride was added, but after the addition a violent reaction took place, the titanium turned dark, the solution coloured, and a greyish precipitate formed around the sample. Further additions of ammonium fluoride restarted a

moderate, sustained reaction. The titanium dissolved completely, leaving a greyish-mauve precipitate, and a solution which became colourless on standing for some time.

25 percent trifluoracetic acid

As before, the reaction first began when ammonium fluoride was added, and was strong and steady. The solution coloured, the titanium turned dark, and a fine white precipitate formed. After the reaction ceased further additions of ammonium fluoride would not restart it. The solution turned colourless after standing for some time.

10 percent trifluoracetic acid

This reaction was practically identical to that seen with the 25 percent trifluoracetic acid, with the one exception of the reactions in all cases being more subdued.

The results of these qualitative tests are summarized in the following Table I. As was anticipated, in all cases where the titanium sample displayed no reaction when exposed to the acid alone, the addition of ammonium or sodium fluoride started an immediate reaction, which in practically all instances continued steadily for a considerable length of time. For a longer period than one would expect the reaction to proceed if only the hydrofluoric acid formed by the additions of ammonium or sodium fluoride was attacking the titanium. Also, in every instance the solution became coloured after the reaction began, indicating the trivalent state of titanium was

present. Then after oxidization by potassium permanganate solution, or by standing exposed to the air, the solutions became colourless, indicating the tetravalent state of titanium.

TABLE Ia

Results of preliminary qualitative tests on Remington Arms, cold rolled, polished titanium.

Reagent	Concentration	Reaction		Solution Coloured
		Alone	NH_4F	
H_2SO_4	2N	None	violent	yes
H_2SO_4	4N	None	strong	yes*
HNO_3	Dilute (4-1)	None	violent	yes
HNO_3	Conc.	None	moderate	yes
HCl	2N	None	strong	yes
$HClO_4$	12%	None	strong	yes
CH_3COOH	50%	None	strong	yes
HCOOH	50%	None	strong	yes
CF_3COOH	100%	None	slight	no
CF_3COOH	75%	None	strong	yes
CF_3COOH	50%	None	violent	yes
CF_3COOH	25%	None	strong	yes
CF_3COOH	10%	None	strong	yes

*sodium fluoride added instead of ammonium fluoride.

Thus it is seen in all cases when ammonium or sodium fluoride

is added to an acid solution in which a titanium sample is not being attacked, a reaction immediately takes place, with the dissolution of the titanium and evolution of hydrogen gas. As there seemed to be no difference in the reaction whether ammonium or sodium fluoride was added, and as a good supply of ammonium fluoride was on hand, of greater purity than the sodium fluoride available, ammonium fluoride was used as the addition agent in all further tests conducted during this investigation.

PART II

SECTION A

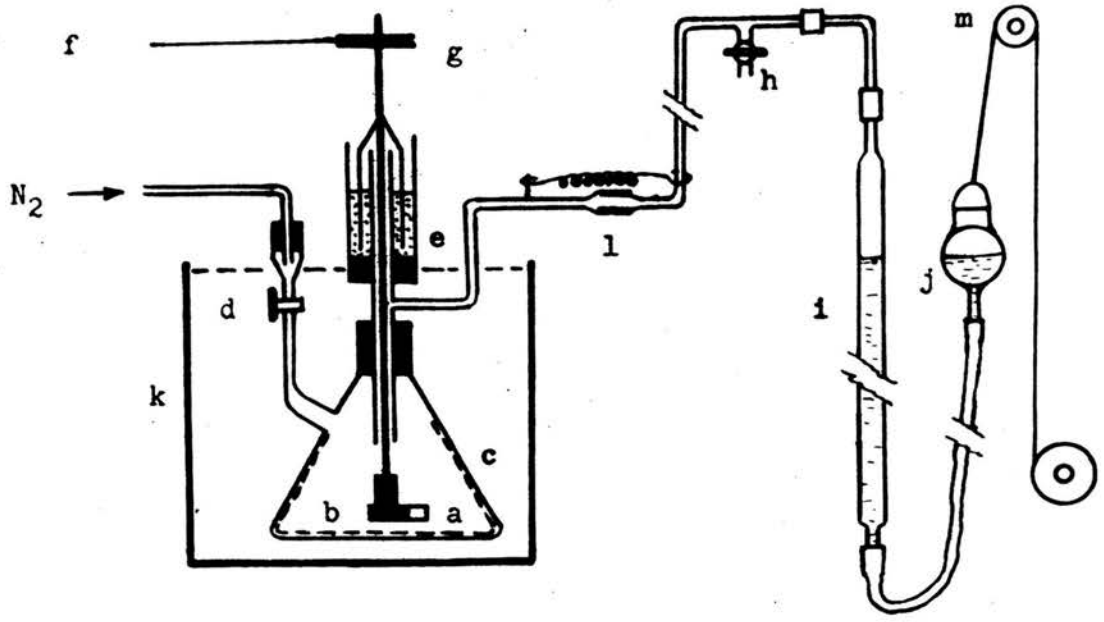
The Rate of Dissolution of Titanium in Different Concentrations of Sulphuric Acid, With the Addition of a Constant Amount of Ammonium Fluoride.

The investigation of the rate of dissolution of titanium in these mixtures was based on the collection and measurement of the hydrogen gas liberated.

(i) Method and Apparatus:

The apparatus for this investigation, as shown in Figure 1, consisted of a flask to hold the titanium sample and acid for dissolution, a stirring mechanism with a mercury seal, a constant temperature water bath, and a burette to collect the evolved hydrogen gas.

The flask used "c" was a two hundred cubic centimeter Erlenmeyer flask, coated inside with paraffin to resist any attack by the hydrofluoric acid formed, and to one side of which a funnel "d" with a valve was attached. This funnel was used to introduce nitrogen gas and reagents into the flask. The stirring mechanism consisted of a vertical glass rod, at the upper end of which was an aluminum driving pulley "g", and at the lower end an ebonite rod wedged unto the glass rod. An ebonite foot "a" with its face inclined at 45 degrees to the vertical and turning in the direction of rotation, could be attached and detached from the bottom of the ebonite rod by means of a tongue

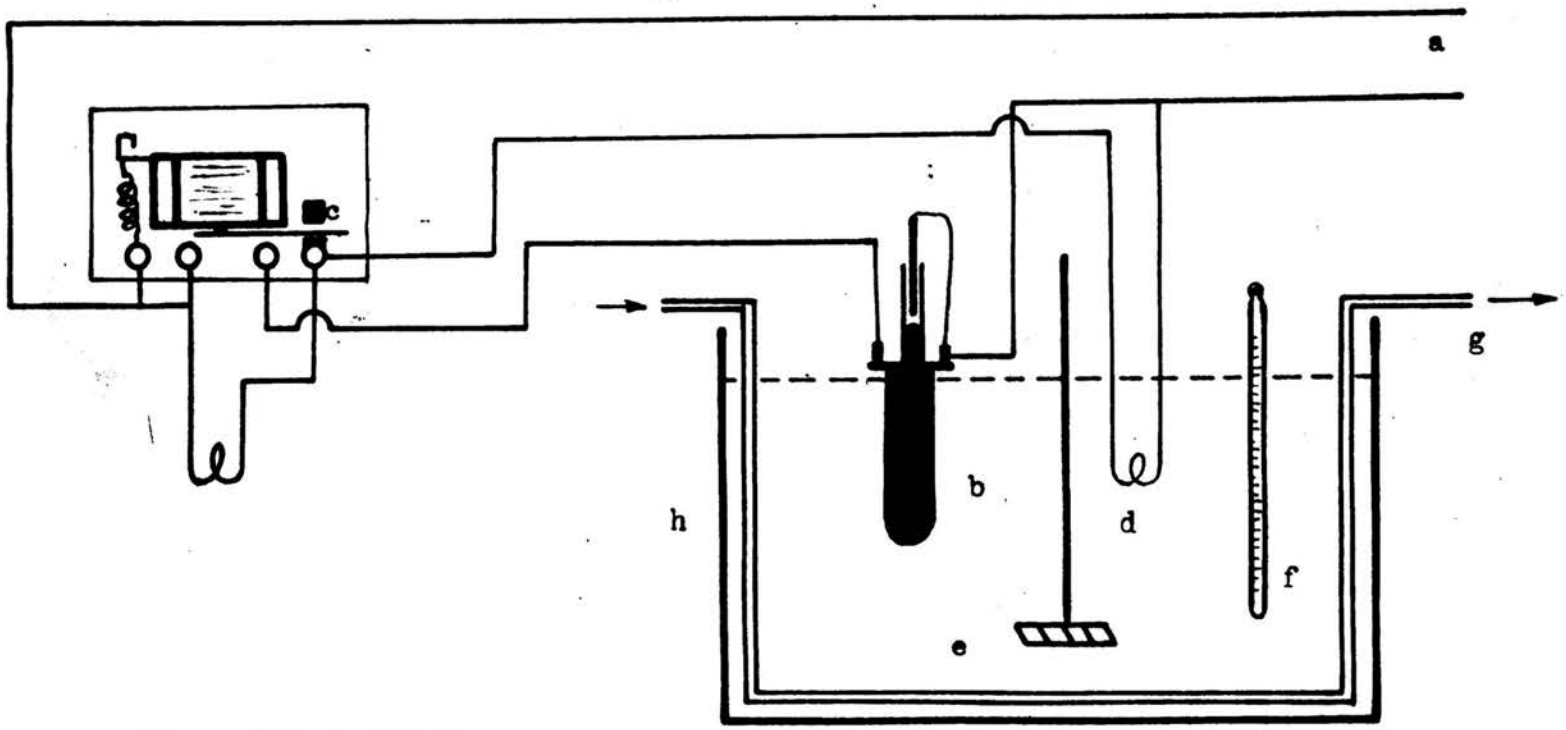


a - Ti sample on foot of stirrer
b - ebonite foot
c - paraffin lined flask
d - funnel for introducing N_2 and reagents
e - mercury seal
f - driving belt
g - driving pulley
h - gas outlet valve
i - gas burette
j - levelling bulb
k - constant temperature water bath
l - spring held ground glass connection
m - levelling bulb pulley system

Figure 1

Apparatus for determining the rate of dissolution of titanium in acids with added ammonium fluoride.

and groove connection. The aluminum driving pulley was connected by a belt to a motor, the speed of which was adjustable by a rheostat. The mercury seal "e" on the shaft permitted free rotation while at the same time it prevented any gas from escaping out through the shaft opening. One side of the tube within which the shaft rotated had an opening, connected by glass tubing to the burette. A ground glass joint "l", held tightly closed by a spring, permitted the flask to be disconnected from the burette tubing. The flask was fitted to the stirring mechanism by a rubber stopper permanently attached to the stirring mechanism, as shown in the Figure 1. The burette "i" used to collect and measure the evolved hydrogen gas was connected by rubber tubing to a levelling bulb "j", which was filled with distilled water. This bulb was raised and lowered by a pulley system "m". Valve "h" could be opened, and was used when the system was being flushed with nitrogen gas, or the gas in the burette displaced by the water from the levelling bulb. The whole flask was submerged in a thermo-regulated water bath at 25° C. (Figure 2). This regulator automatically kept the bath to an accuracy of _0.1° C. The whole system was absolutely air-tight when all the valves were closed, and was tested frequently for any possible leakage by opening valves "d" and "h" and by putting a little gas in under pressure to drive the water level in the burette a few inches below that of the levelling bulb, then closing the two valves and leaving for several hours. At the end of this time if the positive pressure in the system still measured the same as



a - line voltage, 110 V.
b - mercury thermo-regulator
c - solenoid controlled switch
d - heating lamp
e - stirrer
f - thermometer
g - cooling water coil
h - water bath

Figure 2

Water bath with thermo-regulator.

at first, the system was considered gas tight.

(ii) Procedure:

A sample of Remington Arms titanium, cold rolled sheet 1.5 mm. thick and with a nominal purity of over 99 percent, was ground down to exactly 1 centimetre square, and mounted in bakelite using a metallographic specimen mounting press so that only one surface, 1 square centimetre in area, was exposed. The exposed titanium surface was then polished with No. 00 emery paper and the bakelite mounting glued to the horizontal ebonite foot with "plastic cement". The ebonite foot was then slipped on the ebonite bottom of the stirring rod, the Erlenmeyer flask fitted to the stirring mechanism, and the whole submerged in the constant temperature water bath to a depth that the rubber stopper joining the flask and stirring mechanism was completely covered with water. This precaution was taken so that bubbles could be easily spotted if there was any gas leakage around the rubber stopper. The temperature of the water bath was now adjusted to 25°C_0.1°C, using an immersion heating element if the room temperature was below 25° C, and a cooling water coil if above 25° C. Next nitrogen gas from a cylinder was washed through a gas washer containing a solution of twenty grams of pyrogallol in five hundred cubic centimetres of KOH solution (1:2), as recommended by G. Lunge [1], to remove

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1) Lunge, G., Technical Methods of Chemical Analysis, Vol. 1, Part I, 209, D. Van Nostrand and Co., New York, 1908.

oxygen from the nitrogen gas used. This washed, oxygen free nitrogen gas was then directed into the Erlenmeyer flask through valve "d", flushing out the system, and escaping through the open valve "h" to the atmosphere. The nitrogen stream was continued for 15 minutes, and towards the end of this period the air at the top of the burette was also displaced by nitrogen. This was accomplished by first closing the valve "h", then lowering the levelling bulb to draw nitrogen into the burette, then opening valve "h" and raising the levelling bulb to expell the mixture of air and nitrogen in the burette. The operation being repeated several times to make sure all air was displaced. It was necessary to replace the air in the system with nitrogen because M. E. Straumanis and P. C. Chen [2] found if oxygen was present the

2) Straumanis, M. E. and Chen, P. C., The Mechanism and Rate of Dissolution of Titanium in Hydrofluoric Acid, Journal of the Electrochemical Society, 98, 6, 234-240, (1951)

reaction

$$4TiF_3 + 4HF + O_2 \rightarrow 4TiF_4 + 2H_2O \quad (1)$$

took place, with a contraction in volume. Also titanium may act catalytically in the formation of water from oxygen and liberated hydrogen.

One hundred cubic centimetres of sulphuric acid, of chemically pure grade whose concentration had been checked by titration against a standard sodium carbonate solution using a methyl orange indicator, was placed in the Erlenmeyer flask before the nitrogen flush began.

This was sufficient acid to completely cover the titanium sample on the ebonite foot. After the air displacement operation was completed, 0.1855 grams of ammonium fluoride was added to the flask. This amount of ammonium fluoride would give 100 c.c. of 1/20 N hydrofluoric acid, if it were possible for the reaction

$$2NH_4F + H_2SO_4 \rightleftharpoons (NH_4)_2\ SO_4 + 2HF \quad (2)$$

or possibly $NH_4F + H_2SO_4 \rightleftharpoons (NH_4)HSO_4 + HF$

to go to completion. However, the reaction ceases at some equilibrium value, and consequently, the acid mixture is never quite 1/20 N with respect to hydrofluoric acid, though becoming more nearly so as the strength of the H_2SO_4 in the acid mixture is increased. However, during this investigation we are assuming for ease of calculation and explanation that the reaction (2) has gone to completion, and the acid mixture is 1/20 N with respect to hydrofluoric acid.

To avoid any dilution of the H_2SO_4 during the addition of the ammonium fluoride, the NH_4F is first dissolved in distilled water to give a total of 1 c.c. of solution. Then 1 c.c. of H_2SO_4 of double the strength of the 100 c.c. of acid placed in the Erlenmeyer flask is added to this 1 c.c. of solution, giving a total of 2 c.c. of sulphuric acid solution, in which 0.1855 grams of ammonium fluoride are dissolved, of the same strength as the 100 c.c. of acid already in the flask. For example, if the 100 c.c. of acid in the flask is 2N H_2SO_4, then the NH_4F is dissolved in distilled water to give a total volume of 1 c.c. of solution, and 1 c.c. of 4N H_2SO_4 is added to give

a total of 2 c.c. of 2N H_2SO_4. This 2 c.c. of 2N H_2SO_4 containing the ammonium fluoride is added to the 100 c.c. of 2N H_2SO_4 in the Erlenmeyer flask.

The addition is made through valve "d", and the valve immediately closed. The water level in the burette was now quickly adjusted to read zero on the burette scale, valve "h" closed, and the motor driving the rotating mechanism turned on to give the titanium sample immersed in the acid mixture a speed of rotation of 250 revolutions per minute. The reason for stirring the sample in the acid was to help remove the hydrogen gas as soon as it formed on the surface of the metal, to give a better distribution of fresh acid into the reaction interface, and to assist in uniform temperature distribution in the acid.

As the hydrogen gas was evolved from the reaction of the titanium metal with the acid, it passed over into the burette and displaced the water column there. To equalize the gas pressure within the burette and the outside atmospheric pressure, the levelling bulb was constantly lowered to the same water level shown in the burette. The rate of hydrogen evolution in cubic centimetres per minute was observed by recording the volume of gas collected at regular intervals. In order to calculate the volume of hydrogen collected on the basis of standard conditions, room temperature and atmospheric pressure were also recorded.

For several experiments the runs were continued long enough to make sure that all the hydrofluoric acid formed according to reaction

(2) was exhausted, and the dissolution continued after that time was caused by the sulphuric acid present. When this fact had been confirmed, future runs were made only until the peak dissolution rate had been reached and passed. When this stage was reached a final reading was made of the hydrogen collected in the burette, the rotating mechanism was stopped and the flask taken off and dumped. The titanium sample was first rinsed with distilled water to stop the reaction, then dried and examined.

Seven different concentrations of sulphuric acid were investigated, 0.5N, 1N, 2N, 4N, 6N, 8N and 10N. With the amount of ammonium fluoride to each (0.1855 grams NH_4F) to make the solution 1/20N with respect to hydrofluoric acid, assuming that Reaction (2) goes to completion.

(iii) Calculations

The following is a sample calculation using data taken from Table VII, to show how the rates of dissolution were arrived at.

Average room temperature 23.6°C or 296.6°K

Average barometric pressure 729.1 mm. Hg.

Barometric pressure corrections according to C. D. Hodgman's 3) tables.

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3) Hodgman, C. D., Handbook of Chemistry and Physics, Chemical Rubber Publishing Co., Cleveland, 31st edition, (1949)

Correction for water vapour pressure 21.8 mm. Hg

Correction for temperature of the barometer 2.7 mm. Hg

Pressure after corrections 729.1—(21.8 2.7)

= 704.6 mm. Hg.

According to the laws of Boyle and Gay Lussac, the factor from this data to convert the volume of hydrogen gas collected to a volume at standard conditions of temperature and pressure is;

$$\frac{273}{296.6}\ ^{o}K \times \frac{704.6}{760}\ mmHg = 0.852$$

After 120 minutes of running the experiment,

Volume of hydrogen gas collected 4.9 c.c.

Volume of hydrogen gas actually collected at standard conditions of temperature and pressure 4.9 x 0.852

= 4.17 c.c.

The rate of dissolution of the titanium was calculated from the following expression,

$$V_1 = \frac{\Delta\ v_o}{t \times A} \times 1000 \qquad (3)$$

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3) Fontana, M. G., Industrial and Engineering Chemistry, 40, 10, 99-100A, (1948)

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where V_1 the dissolution rate in mm^3/cm^2-min.

v_o the difference in volume of hydrogen gas collected at standard conditions between time intervals in minutes.

t the time interval in minutes, in this case 20 minutes.

A the area of the sample surface in square centimetres, in this case 1 square centimetre.

So, at the same point in the experiment, 120 minutes after the beginning, the rate of dissolution is,

$$V_1 = \frac{0.85}{20 \times 1} \times 1000 = 42.5 \text{ mm}^3/\text{cm}^2\text{-min.}$$

To convert this rate of dissolution from cubic millimetres of hydrogen gas evolved to milligrams of the titanium sample lost, is quite simple. Assuming titanium and hydrogen react in the following manner, according to Evans 4)

$$2Ti + 6H \rightarrow 2T^{+++} + 3H_2 \quad (4)$$

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4) Evans, V. R., Metallic Corrosion Passivity and Protection, Longmans, Green and Co., New York, 255, (1948)

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so

$2Ti \rightarrow 3(22.412)$ litres of H_2

$2(47.9)$ grams $Ti \rightarrow 67.236$ litres of H_2

95.80 grams $Ti \rightarrow 67,236,000$ mm^3 of H_2

$1\ mm^3H_2 \rightarrow \frac{95.80}{67,236,000} = 0.00142$ mg. Ti

Therefore the factor to convert the rate of dissolution from mm^3H_2 to mg. Ti is 0.00142 and at the point in the experiment 120 minutes after the beginning the rate of dissolution is,

$$V_2 = (42.5 mm^3/cm^2\text{-min.} \times 0.00142) = 0.60 \text{ mg}/\text{cm}^2\text{-min.}$$

As was mentioned previously, several tests were made to confirm the fact that dissolution of the titanium sample continued on past the time the hydrofluoric acid formed, according to reaction (2), was ex-

hausted. Which meant that the dissolution was not due entirely to the hydrofluoric acid present, but also in part to the sulphuric acid. As the rate of dissolution was faster with the stronger concentrations of sulphuric acid, these stronger acids were used for this test, for even with them the time consumed was considerable to collect a volume of hydrogen gas evolved greater than would be given off by the hydrofluoric acid alone reacting with the titanium sample. Also, as it was impractical to stay with the experiment the whole time during the 70 or 80 hours a run took, a method was worked out to get an approximate measurement of the hydrogen evolved overnight while the apparatus was left unattended. This method was to turn off the rotating mechanism, but to maintain the constant temperature bath at 25° C. Then barely crack valve "h" so that the hydrogen formed could escape to the atmosphere but maintained a sufficient flow outward through the opening so that a positive pressure of hydrogen was kept in the system. In the morning, the stirring mechanism was turned on, valve "h" closed, and measurements again taken of the hydrogen collected in the burette. The rate of hydrogen evolution for the period when no hydrogen gas was actually collected, was taken as the average rate between the last reading before the apparatus was shut down, and the first reading when it was again started up.

The following is a sample calculation, with data also taken from Table VII, to show how the hydrogen evolved exceeded that which could be expected from the action of hydrofluoric acid alone on

titanium.

Assuming the reaction

$$2HF \rightarrow H_2 \text{ (22.412 litres)} \qquad (5)$$

goes to completion, which is not likely to happen entirely.

Then 1000 c.c., 1N HF $\rightarrow \frac{H_2}{2} = \frac{22.412}{2}$ litres of H_2

so the 100 c.c. of 1/20N HF used in this test will liberate

$$\frac{22.412}{2} \times \frac{1}{20} \times \frac{100}{1000} = \underline{56 \text{ c.c. } H_2}$$

Assuming also that the reaction

$$2NH_4F + H_2SO_4 \rightarrow (NH_4)_2\ SO_4 + 2HF$$

or $$NH_4F + H_2SO_4 \rightarrow (NH_4)HSO_4 + HF$$

goes to completion and the acid mixture is 1/20N with respect to HF.

Taking data from Table VII

Average temperature for whole run	21.6°C or 294.6°K
Average barometric pressure for whole run	728.5 mm Hg.
Correction for water vapour pressure	19.3 mm Hg.
Correction for temperature of the barometer	2.6 mm Hg.
Pressure after corrections	728.5-(19.3+2.6) = 706.6 mm Hg.
Amount of H_2 collected after 400 minutes	<u>13.18 c.c. H_2</u>
Rate of collection of H_2 at 400 minutes	0.51 c.c. per 20 min.
Rate of collection of H_2 at 1240 minutes	0.42 c.c. per 20 min.
Time interval	840 min. or 42, 20 min. intervals

H_2 supposed collected for 1st half of period when apparatus shut down $\frac{42}{2} \times 0.51 = 10.71$c.c.$H_2$

H_2 supposed collected for 2nd half of period when apparatus shut down $\frac{42}{2} \times 0.42 = 8.82$c.c.$H_2$

Amount of H_2 collected from 1240 to 1320 min. 1.70 c.c. H_2

Rate of collection of H_2 at 1320 minutes 0.42 c.c. per 20 min.

Rate of collection of H_2 at 2900 minutes 0.26 c.c. per 20 min.

Time interval 1580 minutes or 79, 20 minute intervals

H_2 supposed collected for 1st half of period when apparatus shut down $\frac{79}{2} \times 0.42 = \underline{16.59}$c.c.$H_2$

H_2 supposed collected for 2nd half of period when apparatus shut down $\frac{79}{2} \times 0.26 = \underline{10.27}$c.c.$H_2$

Amount of H_2 collected from 2900 to 2960 minutes 0.78c.c.H_2

Rate of collection of H_2 at 2960 minutes 0.26 c.c. per 20 min.

Rate of collection of H_2 at 4060 minutes 0.18 c.c. per 20 min.

Time interval 1100 minutes, or 55, 20 minute intervals

H_2 supposed collected for 1st half of period when apparatus shut down $\frac{55}{2} \times 0.26 = \underline{7.15}$ c.c.H_2

H_2 supposed collected for 2nd half of period when apparatus shut down $\frac{55}{2} \times 0.18 = \underline{4.95}$ c.c.H_2

Amount of H_2 collected from 4060 to 4140 minutes $\underline{0.70}$ c.c.H_2

Total amount of H_2 collected (13.18 + 10.71 + 8.82 + 1.70 + 16.59 + 10.27 + 0.78 + 7.15 + 4.95 + 0.70)cc.H_2

= 74.85 c.c. H_2

This 74.85 c.c. H_2 is considerably more than the 56 c.c. expected to be evolved by the action of hydrofluoric acid alone on the titanium, so the difference, 74.85-56 = 18.85 c.c. H_2, must be from the action of sulphuric acid on the titanium.

(iv) Results:

It was seen on plotting the average maximum rates of dissolution against the concentrations of the sulphuric acid in normalities, as shown in Figure 3, that the rate of dissolution increased in almost a straight line ratio as the concentration of the sulphuric acid increased. From the rates of dissolution tabulated in Tables I to XIV it was noted in 2N, 4N and 6N sulphuric acid the rate of dissolution started with a short induction period, gradually reached its maximum, then slowly tapered off. While with the 0.5N, 1N, 8N and 10N sulphuric acid the maximum dissolution rate was attained almost with the first reading, and a decline followed from there. There was no great difference in the rate of decrease of the dissolution rate from the maximum in any of the sulphuric acid concentrations. In every case after dissolution the sample surfaces had a dull grey, pebbley finish, in contrast to their bright, polished surface before the experiment began.

Table I, Rate of dissolution of Ti in 0.5N H_2SO_4 plus 1/20N NH_4F

Run No. 1

Time (Min.)	Volume H_2 (c.c.)	Volume (c.c.)	Rate mm^3/cm^2-min.	Rate mg/cm^2-min.	Temp °C Average	Corrected Pressure
30	1.31	1.31	43.7	.62	21.5	716.5
60	2.27	.96	32.0	.45		mm Hg
90	3.15	.88	29.3	.42		
120	4.19	1.04	34.8	.49		
150	5.24	1.05	35.0	.50		
180	6.20	.96	32.0	.45		
210	7.17	.97	32.3	.46		
240	8.13	.96	32.0	.45		
270	9.00	.87	29.0	.41		
300	9.79	.79	26.3	.37		
330	10.57	.78	26.0	.37		
360	11.40	.83	27.7	.39		
390	12.19	.79	26.3	.37		
420	13.02	.83	27.7	.39		
450	13.74	.72	24.0	.34		
480	14.46	.72	24.0	.34		
510	15.18	.72	24.0	.34		
540	15.91	.73	24.3	.34		
570	16.74	.83	27.7	.39		
600	17.35	.61	20.3	.29		

Average maximum rates run No. 1: 29.37 mm^3/cm^2-min. and 0.415 mg./cm^2-min.

Table II, Rate of dissolution of Ti in 0.5N H_2SO_4 plus 1/20N NH_4F

Run No. 2

Time (Min.)	Volume H_2 (c.c.)	Volume (c.c.)	Rate mm^3/cm^2-min.	Rate mg/cm^2-min.	Temp °C Average	Corrected Pressure
30	1.32	1.32	44.0	0.62	21.2	721.2
60	2.29	.97	32.3	0.46		mm Hg
90	3.17	.88	29.3	0.42		
120	4.23	1.06	35.3	0.50		
150	5.19	.96	32.0	0.45		
180	6.07	.88	29.3	0.42		
210	6.95	.88	29.3	0.42		
240	7.84	.89	29.7	0.42		
270	8.72	.88	29.3	0.42		
300	9.60	.88	29.3	0.42		
330	10.48	.88	29.3	0.42		
360	11.14	.66	22.0	0.31		
390	11.89	.75	25.0	0.35		
420	12.63	.74	24.7	0.35		
450	13.38	.75	25.0	0.35		
480	14.13	.75	25.0	0.35		
510	14.88	.75	25.0	0.35		
540	15.54	.66	22.0	0.31		

Average maximum rates run No. 2: 29.16 mm^3/cm^2-min. and 0.413 mg./cm^2-min.

Average maximum rates for both runs: 29.26 mm^3/cm^2-min. and 0.414 mg./cm^2-min.

Table III, Rate of dissolution of Ti in 1N H_2SO_4 plus 1/20N NH_4F

Run No. 1

Time (Min.)	Volume H_2 (c.c.)	Volume (c.c.)	Rate (mm^3/cm^2-min.)	Rate (mg/cm^2-min.)	Temp °C (Avg.)	Corrected Pressure
30	1.05	1.05	35.0	.49	21.75	716.7
60	1.88	.83	27.7	.39		mm Hg
90	2.77	.89	29.7	.42		
120	3.67	.90	30.0	.43		
150	4.54	.87	29.0	.41		
180	5.32	.78	26.0	.37		
210	6.07	.75	25.0	.35		
240	6.90	.83	27.7	.39		
270	7.68	.78	26.0	.37		
300	8.47	.79	26.3	.37		
330	9.12	.65	21.7	.31		
360	9.84	.72	24.0	.34		

Average maximum rates run No. 1: 28.24 mm^3/cm^2-min. and 0.399 mg./cm^2-min.

Table IV, Rate of Dissolution of Ti in 1N H_2SO_4 plus 1/20N NH_4F

Run No. 2

Time (Min.)	Volume H_2 (c.c.)	Volume (c.c.)	Rate (mm^3/cm^2-min.)	Rate (mg/cm^2-min.)	Temp °C (Avg.)	Corrected Pressure
30	1.22	1.22	40.7	0.58	23.0	716.6
60	2.09	.87	29.0	0.41		mm Hg
90	2.96	.87	29.0	0.41		
120	3.87	.91	30.3	0.43		
150	4.78	.91	30.3	0.43		
180	5.74	.96	32.0	0.45		
210	6.52	.78	26.0	0.37		
240	7.35	.83	27.7	0.39		
270	8.18	.83	27.7	0.39		
300	9.09	.91	30.3	0.43		
330	9.92	.83	27.7	0.39		
360	10.73	.81	27.0	0.38		
390	11.54	.81	27.0	0.38		
420	12.35	.81	27.0	0.38		
450	13.05	.70	23.3	0.33		
480	13.79	.74	24.7	0.35		

Average maximum rates run No. 2: 29.41 mm^3/cm^2-min. and 0.4157 mg./cm^2-min.

Average maximum rates for both runs: 28.825 mm^3/cm^2-min. and 0.4075 mg./cm^2-min.

Table V, Rate of Dissolution of Ti in 2N H_2SO_4 plus 1/20N NH_4F

Run No. 1

Time (Min.)	Volume H_2 (c.c.)	Volume (c.c.)	Rate (mm^3/cm^2-min.)	Rate (mg/cm^2-min.)	Temp °C (Avg.)	Corrected Pressure
20	.53	.53	26.5	.38	21.4	717.1
40	1.05	.52	26.0	.37		mm Hg
60	1.66	.61	30.5	.43		
80	2.21	.55	27.5	.39		
100	2.77	.56	28.0	.40		
120	3.33	.56	28,0	.40		
140	3.83	.50	25.0	.36		
160	4.35	.52	26.0	.37		
180	4.87	.52	26.0	.37		
200	5.31	.44	22.0	.31	22.3	715.3
220	5.92	.61	30.5	.43		mm Hg
240	6.44	.52	26.0	.37		
260	6.87	.43	21.5	.30		
280	7.31	.44	22.0	.31		

Average maximum rates run No. 1: 26.95 mm^3/cm^2-min. and 0.383 $mg./cm^2$-min.

Table VI, Rate of Dissolution of Ti in 2N H_2SO_4 plus 1/20N NH_4F

Run No. 2

Time (Min.)	Volume H_2 (c.c.)	Volume (c.c.)	Rate (mm^3/cm^2-min.)	Rate (mg/cm^2-min.)	Temp °C (Avg.)	Corrected Pressure
20	.35	.35	17.5	.25	22.5	714.8
40	.69	.34	17.0	.24		mm Hg
60	1.12	.43	21.5	.30		
80	1.70	.58	29.0	.41		
100	2.27	.57	28.5	.40		
120	2.85	.58	28.0	.40		
140	3.46	.61	30.5	.43		
160	4.07	.61	30.5	.43		
180	4.76	.69	34.5	.49		
200	5.54	.69	34.5	.49		
220	6.14	.69	34.5	.49		
240	6.66	.52	26.0	.37		
260	7.35	.69	34.5	.49		
280	8.04	.69	34.5	.49		
300	8.65	.61	30.5	.43		
320	9.09	.44	22.0	.31		

Average maximum rates run No. 2: 31.36 mm^3/cm^2-min., and 0.444 mg./cm^2-min.

Average maximum rates for both runs: 29.66 mm^3/cm^2-min., and 0.4135 mg./cm^2-min.

Table VII, Rate of Dissolution of Ti in 4N H_2SO_4 plus 1/20N NH_4F

Run No. 1

Time (Min.)	Volume H_2 (c.c.)	Volume (c.c.)	Rate (mm^3/cm^2-min.)	Rate (mg/cm^2-min.)	Temp °C (Avg.)	Corrected Pressure
20	.60	.60	30.0	.43	21.6	706.6
40	1.11	.51	25.5	.36		mm Hg
60	1.70	.59	29.5	.42		
80	2.47	.77	38.5	.55		
100	3.32	.85	42.5	.60		
120	4.17	.85	42.5	.60		
140	4.94	.77	38.5	.55		
160	5.62	.68	34.0	.48		
180	6.48	.86	43.0	.61		
200	7.07	.59	29.5	.42		
220	7.84	.77	38.5	.55		
240	8.43	.59	29.5	.42		
260	9.10	.67	33.5	.48		
280	9.72	.62	31.0	.44		
300	10.34	.62	31.0	.44		
320	10.96	.62	31.0	.44		
340	11.47	.51	25.5	.36		
360	11.98	.51	25.5	.36		
380	12.67	.69	39.5	.56		
400	13.18	.51	25.5	.36		
1240	0	0	0	0		
1260	.51	.51	25.5	.36		
1280	.85	.34	17.0	.24		
1300	1.27	.42	21.0	.30		
1320	1.70	.43	21.5	.30		
2900	23.76	0	0	0		
2920	24.02	.26	13.0	.18		
2940	24.29	.26	13.0	.18		
2960	24.54	.26	13.0	.18		

Table VII continued

4060	0	0	0	0
4080	.18	.18	9.0	.13
4100	.53	.35	17.5	.25
4120	.71	.18	9.0	.13
4140	.88	.17	8.5	.12

Total 74.85 c.c.

Average maximum rates run No. 1: 38.38 mm^3/cm^2-min., and 0.545 mg/cm^2-min.

Table VIII, Rate of Dissolution of Ti in 4N H_2SO_4 plus 1/20N NHF_4

Run No. 2

Time (Min.)	Volume H_2 (c.c.)	Volume (c.c.)	Rate (mm^3/cm^2-min.)	Rate (mg/cm^2-min.)	Temp °C (Avg.)	Corrected Pressure
30	.26	.26	8.9	.13	21.4	712.8
60	.87	.61	20.3	.29		mm Hg
90	1.73	.86	28.7	.31		
120	2.59	.86	28.7	.31		
150	3.45	.86	28.7	.31		
180	4.32	.87	29.0	.41		
210	5.20	.88	29.3	.42		
240	6.06	.86	28.7	.31		
270	6.93	.87	29.0	.41		
300	7.79	.86	28.7	.31		
330	8.57	.78	26.0	.37		
360	9.35	.78	26.0	.37		
390	10.05	.70	23.3	.33		
420	10.74	.69	23.0	.33		

Average maximum rates run No. 2: 28.28 mm^3/cm^2-min., and 0.353 mg/cm^2-min.

Average maximum rates for both runs: 33.33 mm^3/cm^2-min., and 0.449 $mg./cm^2$-min.

Table IX, Rate of Dissolution of Ti in 6N H_2SO_4 plus 1/20N NH_4F

Run No. 1

Time (Min.)	Volume H_2 (c.c.)	Volume (c.c.)	Rate (mm^3/cm^2-min.)	Rate (mg/cm^2min.)	Temp°C (Avg.)	Corrected Pressure
30	.69	.69	13.0	.18	23.8	710.6
60	1.67	.98	32.7	.46		mm Hg
90	2.75	1.08	36.0	.51		
120	3.95	1.20	40.0	.57		
150	4.98	1.03	34.3	.49		
180	6.01	1.03	34.3	.49		
210	7.04	1.03	34.3	.49		
240	8.24	1.20	40.0	.57		
270	9.27	1.03	34.3	.49		
300	10.28	1.01	33.7	.48		
330	11.14	.86	28.7	.41		
360	12.00	.86	28.7	.41		
390	12.68	.68	22.7	.32		
420	13.37	.69	23.0	.33		
1380	0	0	0	0		
1410	.78	.78	26.0	.37		
1440	1.47	.69	23.0	.33		
1470	2.07	.60	20.0	.28		
1500	2.68	.59	19.7	.28		
1530	3.37	.69	23.0	.33		
1560	3.97	.60	20.0	.28		
1590	4.62	.65	21.7	.31		
1620	5.27	.65	21.7	.31		
1650	5.88	.61	20.3	.29		
1680	6.44	.56	18.7	.27		
2940	0	0	0	0		
2970	.43	.43	14.3	.20		
3000	.86	.43	14.3	.20		
Total	62.4 c.c.					

Average maximum rates run No. 1: 35.51 mm^3/cm^2-min., and 0.505 mg/cm^2-min.

Table X, Rate of Dissolution of Ti in 6N H_2SO_4 plus 1/20N NH_4F

Run No. 2

Time (Min.)	Volume H_2 (c.c.)	Volume (c.c.)	Rate (mm^3/cm^2-min.)	Rate (mg/cm^2-min.)	Temp °C (Avg.)	Corrected Pressure
30	.69	.69	23.0	.33	22.7	708.0
60	1.38	.69	23.0	.33		mm Hg
90	2.32	.94	31.3	.44		
120	3.61	1.29	43.0	.61		
150	4.87	1.26	42.0	.60		
180	6.12	1.25	41.7	.59		
210	7.40	1.28	42.7	.61		
240	8.60	1.20	40.0	.57		
270	9.55	.95	31.7	.45		
300	10.54	.99	33.0	.47		
330	11.48	.94	31.3	.44		
360	12.26	.78	26.0	.37		
390	12.99	.73	24.3	.35		

Average maximum rates run No. 2: 37.41 mm^3/cm^2-min., and 0.531 mg/cm^2-min.

Average maximum rates for both runs: 36.46 mm^3/cm^2-min., and 0.518 mg/cm^2-min.

Table XI, Rate of Dissolution of Ti in 8N H_2SO_4 plus 1/20N NH_4F

Run No. 1

Time (Min.)	Volume H_2 (c.c.)	Volume (c.c.)	Rate (mm^3/cm^2-min.)	Rate (mg/cm^2-min.)	Temp °C (Avg.)	Corrected Pressure
30	1.12	1.12	37.3	.53	22.5	712.1 mm Hg
60	2.16	1.04	34.3	.49		
90	3.31	1.15	38.3	.54		
120	4.46	1.15	38.3	.54		
150	5.62	1.16	38.7	.55		
180	6.75	1.13	37.7	.54		
210	7.87	1.12	37.3	.53		
240	9.00	1.13	37.7	.54		
270	10.03	1.03	34.3	.49		
300	11.12	1.09	36.3	.52		
330	12.28	1.16	38.7	.55		
360	13.40	1.12	37.3	.53		
1320	0	0	0	0		
1350	.87	.87	29.0	.41		
1380	1.69	.82	27.3	.39		
1410	2.51	.82	27.3	.39		
1440	3.29	.78	26.0	.37		
1470	4.16	.87	29.0	.41		
1500	4.94	.78	26.0	.37		
2760	0	0	0	0		
2790	.61	.61	20.3	.29		
2820	1.22	.61	20.3	.29		

Total 78 c.c. H_2

Average maximum rates run No. 1: 35.52 mm^3/cm^2-min., and 0.53 mg/cm^2-min.

Table XII, Rate of Dissolution of Ti in 8N H_2SO_4 plus 1/20 N NH_4F

Run No. 2

Time (Min.)	Volume H_2 (c.c.)	Volume (c.c.)	Rate (mm^3/cm^2-min.)	Rate (mg/cm^2-min.)	Temp °C (Avg.)	Corrected Pressure
30	.91	.91	30.3	.43	23.1	716.3
60	2.12	1.21	40.3	.57		mm Hg
90	3.25	1.13	37.7	.54		
120	4.39	1.14	38.0	.54		
150	5.54	1.15	38.3	.54		
180	6.66	1.12	37.3	.53		
210	7.79	1.13	37.7	.54		
240	8.91	1.12	37.3	.53		
270	10.03	1.12	37.3	.53		
300	11.07	1.04	34.7	.49		
330	12.11	1.04	34.7	.49		

Average maximum rates run No. 2: 37.99 mm^3/cm^2-min., and 0.540 mg/cm^2-min.

Average maximum rates for both runs: 36.75 mm^3/cm^2-min., and 0.525 mg/cm^2-min.

Table XIII, Rate of Dissolution of Ti in 10N H_2SO_4 plus 1/20N NH_4F

Run No. 1

Time (Min.)	Volume H_2 (c.c.)	Volume (c.c.)	Rate (mm^3/cm^2-min.)	Rate (mg/cm^2-min.)	Temp °C (Avg.)	Corrected Pressure
30	1.30	1.30	43.3	.61	21.8	710.2
60	2.64	1.34	44.7	.63		mm Hg
90	3.98	1.34	44.7	.63		
120	5.23	1.25	41.7	.59		
150	6.44	1.21	40.3	.57		
180	7.66	1.22	40.7	.58		
210	8.87	1.21	40.3	.57		
240	10.08	1.21	40.3	.57		
270	11.23	1.15	38.3	.54		
300	12.37	1.14	38.0	.54		
330	13.67	1.30	43.3	.61		
360	14.88	1.21	40.3	.57		
390	16.00	1.12	37.3	.53		
420	17.13	1.13	37.7	.54		

Average maximum rates run No. 1: 41.33 mm^3/cm^2-min., and 0.58 mg/cm^2-min.

Table XIV, Rate of Dissolution of Ti in 10N H_2SO_4 plus 1/20N NH_4F

Run No. 2

Time (Min.)	Volume H_2 (c.c.)	Volume (c.c.)	Rate (mm^3/cm^2-min.)	Rate (mg/cm^2-min.)	Temp °C (Avg.)	Corrected Pressure
30	1.10	1.10	36.7	.52	24.4	704.0
60	2.42	1.32	44.0	.62		
90	3.74	1.32	44.0	.62		
120	5.12	1.38	46.0	.65		
150	6.50	1.38	46.0	.65		
180	7.86	1.36	45.3	.64		
210	9.18	1.32	44.0	.62		
240	10.45	1.27	42.3	.60		
270	11.64	1.19	39.7	.56		
300	12.83	1.19	39.7	.56		
330	14.02	1.19	39.7	.56		
360	15.21	1.19	39.7	.56		
390	16.49	1.28	42.7	.56		
420	17.76	1.27	42.3	.60		
450	18.91	1.15	38.3	.54		
480	20.10	1.19	39.7	.56		

Average maximum rates run No. 2: 42.7 mm^3/cm^2-min., and 0.60 mg/cm^2-min.

Average maximum rates for both runs: 42.0 mm^3/cm^2-min., and 0.59 mg/cm^2-min.

(V) Conclusions:

It was shown that the reaction between sulphuric acid and titanium was a straight line ratio, plotted on the basis of the rate of dissolution of the titanium against the concentration of the sulphuric acid. Rates of dissolution were much higher in the sulphuric acid with ammonium fluoride added, than in sulphuric acid alone, and rates of dissolution for titanium as high as 0.61 mg/cm^2-min. were obtained in only two hours time in 6N H_2SO_4 plus 0.1855 grams of NH_4F, as compared with maximum rates of only 0.04 mg/cm^2-hr. after 665 hours in 6N H_2SO_4 alone, obtained by other investigators [5] using the same Remington

5) Straumanis, M. E., and Chen, P. C., The Corrosion of Titanium in Acids, Corrosion, 7, 7, 229-237, (1951)

Arms titanium. Apparently, the ammonium fluoride added to the sulphuric acid, thus forming hydrofluoric acid, attacked the corrosion resistant film on the titanium, removed it and permitted the titanium to be much more readily attacked than when subjected to sulphuric acid alone. This would agree with the pore theory of Müller [6], stating

6) Müller, W. J., and Low, E., Zur Theorie der Korrosienserscheinungen, Z. Electrochem., 42, 789, (1936)

that protective films are porous so that the metal is partially protected by the film and partially exposed through the pores to the corroding medium. Then, when the pores become widened as in this case

by hydrofluoric acid dissolving the protective film, the underlying local cells are exposed to the solution (H_2SO_4) and dissolution speeds up. The slope of the curve obtained from plotting rates of dissolution against the normalities of pure H_2SO_4 given by Straumanis and Chen [4] is $\frac{.002}{1}$ between 3N and 4N, $\frac{.008}{1}$ between 4N and 5N, and $\frac{.055}{1}$ between 5N and 6N H_2SO_4. For the straight line relationship between the rate of dissolution and normality of H_2SO_4 plus NH_4F, the equation of the line is $y-1.13x-24.3=0$ and the slope is $\frac{4.52}{4}$. Consequently, the rate of dissolution with increasing normalities of H_2SO_4 plus NH_4F was increasing much more rapidly than was the rate of dissolution in H_2SO_4 alone.

PART II

SECTION B

The Rate of Dissolution of Titanium in a Constant Concentration of Sulphuric Acid, with the Addition of Varying Amounts of Ammonium Fluoride.

As before, the investigation of the rate of dissolution of titanium in these acid mixtures was based on the collection and measurement of the hydrogen gas liberated.

(i) Method and Apparatus:

The method of procedure and apparatus for this investigation was similar to that used in SECTION A where the rate of dissolution in various concentrations of sulphuric acid with the addition of a constant amount of ammonium fluoride was studied.

(ii) Procedure:

The procedure used was also similar to that of SECTION A, using the same method of collecting the hydrogen evolved in a burette. However, in this case no tests were run to confirm that titanium is attacked by sulphuric acid after the hydrofluoric acid present has been exhausted. It was felt that the several tests made previously in SECTION A to show this were sufficient.

Six different concentrations of ammonium fluoride, 0.1855, 0.371, 0.742, 1.855, 3.71 and 7.42 grams, were added to 4N H_2SO_4 to

give respectively 1/20N, 1/10N, 1/5N, 1/2N, 1N and 2N strengths of hydrofluoric acid in 100 c.c. of solution. Assuming in this case also, as was assumed in SECTION A, it is possible that the reaction

$$2NH_4F + H_2SO_4 \rightarrow (NH_4)_2\ SO_4 + 2HF \quad (2)$$

or $$NH_4F + H_2SO_4 \rightarrow (NH_4)HSO_4 + HF$$

goes to completion.

(iii) Calculations:

Calculations were made similar to those explained in detail in SECTION A, to give the rate of dissolution of the one square centimetre sample surface in mm^3/cm^2-min. of hydrogen gas evolved and mg/cm^2-min. of titanium dissolved.

(iv) Results

It was seen on plotting the average maximum dissolution rates against the concentrations of hydrofluoric acid formed on adding ammonium fluoride to 4N H_2SO_4, as shown in Figure 4, that the rate of dissolution increased sharply as the amounts of ammonium fluoride added were increased. The rates were lower than those found by M. E. Straumanis and P. C. Chen [2] for the dissolution of titanium in hydrofluoric acid

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2) Straumanis, M. E., and Chen, P. C., The Mechanism and Rate of Dissolution of Titanium in Hydrofluoric Acid, Journal of the Electrochemical Society, 98, 6, 234-40, (1951)

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alone, of corresponding strengths. Though both curves follow a somewhat similar pattern in that above 0.5N NH_4F they are both in a

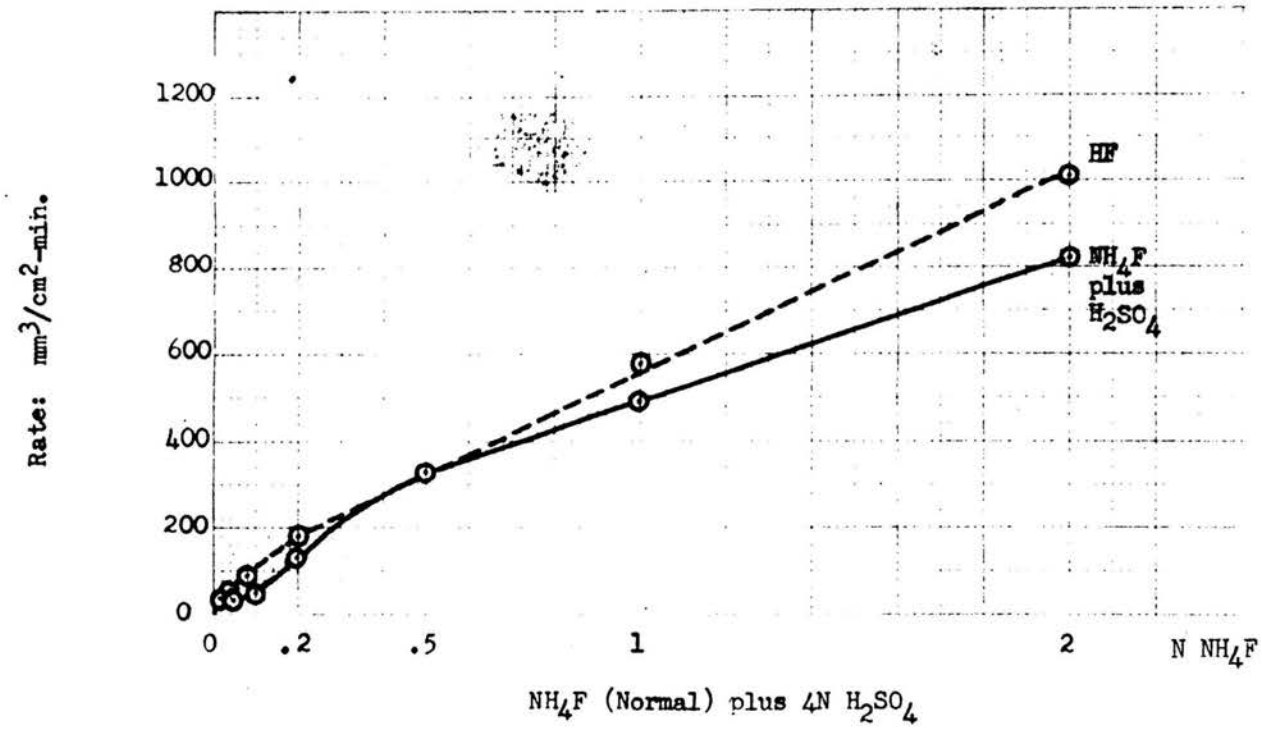

Figure 4

Rate of dissolution of titanium in a constant concentration of H_2SO_4 plus varying amounts of NH_4F.

straight line relationship between the rate of dissolution and the concentration of the acid, and below 0.5N NH_4F both are curved lines. The dissolution rate increased more rapidly in the pure HF than in the 4N H_2SO_4 with NH_4F added, the equation of the straight line portion of the pure HF curve being y-459 -129 0, and the slope $\frac{459}{1}$; and the equation of the straight line portion of the 4N H_2SO_4 NH_4F curve being y-322•79x -173.9 = 0, and the slope $\frac{323}{1}$. Comparing the two slopes, the rate of dissolution in pure HF was increasing approximately 30% faster. The closest point of agreement between the two curves is at 0.5N HF, with a divergence of the curves at values above and below this. From the rates of dissolution given in Tables XV to XXII, it was seen in all cases that the maximum rate of dissolution was reached quickly, generally within the first few readings, then that the rate sustained for a time and finally gradually decreased. Also in every case, after dissolution the titanium sample surface had a dull, pebbley finish.

Table XV

The rate of dissolution of Ti in 4N H_2SO_4 plus 1/20N NH_4F

Run No. 1

Time (Min.)	Volume H_2 (c.c.)^2	Volume (c.c.)	Rate (mm^3/cm^2-min.)	Rate (mg/cm^2-min.)	Temp °C (Avg.)	Pressure Corrected
20	.60	.60	30.0	.43	21.6	706.6
40	1.11	.51	25.5	.36		mm Hg
60	1.70	.59	29.5	.42		
80	2.47	.77	38.5	.55		
100	3.32	.85	42.5	.60		
120	4.17	.85	42.5	.60		
140	4.94	.77	38.5	.55		
160	5.62	.68	34.0	.48		
180	6.48	.86	43.0	.61		
200	7.07	.59	29.5	.42		
220	7.84	.77	38.5	.55		
240	8.43	.59	29.5	.42		

Average maximum rates run No. 1: 38.38 mm^3/cm^2-min. and 0.545 mg/cm^2-min.

Table XVI

The rate of dissolution of Ti in 4N H_2SO_4 plus 1/20N NH_4F

Run No. 2

Time (Min.)	Volume H_2 (c.c.)	Volume (c.c.)	Rate (mm^3/cm^2-min.)	Rate (mg/cm^2-min.)	Temp °C (Avg.)	Pressure Corrected
30	.26	.26	8.9	.13	21.4	712.8
60	.87	.61	20.3	.29		mm Hg.
90	1.73	.86	28.7	.31		
120	2.59	.86	28.7	.31		
150	3.45	.86	28.7	.31		
180	4.32	.87	29.0	.41		
210	5.20	.88	29.3	.42		
240	6.06	.86	28.7	.31		
270	6.93	.87	29.0	.41		
300	7.79	.86	28.7	.31		
330	8.57	.78	26.0	.37		
360	9.35	.78	26.0	.37		
390	10.05	.70	23.3	.33		

Average maximum rates run No. 2: 28.28 mm^3/cm^2-min. and 0.353 mg/cm^2-min.

Average maximum rates for both runs: 33.33 mm^3/cm^2-min. and 0.449 mg/cm^2-min.

Table XVII

The rate of dissolution of Ti in 4N H_2SO_4 plus 1/10N NH_4F

Run No. 1

Time (Min.)	Volume H_2 (c.c.)	Volume (c.c.)	Rate (mm^3/cm^2-min.)	Rate (mg/cm^2-min.)	Temp °C (Avg.)	Corrected Pressure
30	1.57	1.57	52.3	.74	21.25	713.5
60	3.13	1.56	52.0	.74		mm Hg
90	4.62	1.49	49.7	.70		
120	6.01	1.39	46.3	.66		
150	7.60	1.59	53.0	.74		
180	9.19	1.59	53.0	.74		
210	10.71	1.52	50.7	.72		
240	12.19	1.48	49.3	.70		
270	13.67	1.48	49.3	.70		
300	15.15	1.48	49.3	.70		
330	16.55	1.40	46.7	.66		
360	17.94	1.39	46.3	.66		

Run No. 2

30	1.46	1.46	48.7	.69	21.65	706.85
60	2.84	1.38	46.0	.65		mm Hg
90	4.18	1.34	44.7	.63		
120	5.47	1.29	43.0	.61		
150	6.77	1.30	43.3	.61		
180	7.97	1.20	40.0	.57		
210	9.22	1.25	41.7	.59		
240	10.34	1.12	37.3	.53		
270	11.55	1.21	40.3	.57		

Average maximum rates for Run No. 1: 50.145 mm^3/cm^2-min., and 0.709 mg/cm^2-min.

Average maximum rates for Run No. 2: 42.78 mm^2/cm^2-min., and 0.655 mg/cm^2-min.

Average maximum rates for both runs: 46.46 mm^2/cm^2-min., and 0.682 mg/cm^2-min.

Table XVIII

The rate of dissolution of Ti in 4N H_2SO_4 plus 1/5N NH_4F

Run No. 1

Time (Min.)	Volume H_2 (c.c.)	Volume (c.c.)	Rate (mm^3/cm^2-min.)	Rate (mg/cm^2-min.)	Temp °C (Avg.)	Pressure Corrected
30	3.67	3.67	122.3	1.74	23.35	720.7
60	7.51	3.84	128.0	1.82		mm Hg
90	11.22	3.71	123.7	1.76		
120	15.10	3.88	129.3	1.84		
150	19.03	3.93	131.0	1.86		
180	22.70	3.67	122.3	1.74		
210	26.36	3.66	122.0	1.73		
240	30.03	3.67	122.3	1.74		
270	33.7	3.67	122.3	1.74		
300	37.1	3.40	113.3	1.61		
330	40.59	3.49	116.3	1.65		

Run No. 2

30	4.02	4.02	134.0	1.90	22.6	720.4
60	8.05	4.03	134.0	1.91		mm Hg
90	12.25	4.20	140.0	1.99		
120	16.54	4.29	143.0	2.03		
150	20.74	4.20	140.0	1.99		
180	25.02	4.28	142.7	2.03		
210	28.87	3.85	128.3	1.82		
240	32.90	4.03	134.3	1.91		
270	36.66	3.76	125.3	1.78		
300	40.51	3.85	128.3	1.82		
330	44.19	3.68	122.7	1.74		

Average maximum rates for Run No. 1: 122.98 mm^3/cm^2-min., and 1.748 mg/cm^2-min.

Average maximum rates for Run No. 2: 133.90 mm^3/cm^2-min., and 1.902 mg/cm^2-min.

Average maximum rates for both runs: 128.44 mm^3/cm^2-min., and 1.825 mg/cm^2-min.

Table XIX

The rate of dissolution of Ti in 4N H_2SO_4 plus 1/2N NH_4F

Run No. 1

Time (Min.)	Volume H_2 (c.c.)	Volume (c.c.)	Rate (mm^3/cm^2-min.)	Rate (mg/cm^2-min.)	Temp °C (Avg.)	Pressure Corrected
15	4.88	4.88	325.3	4.62	26.0	700.46
30	9.84	4.96	330.7	4.69		mm Hg
45	14.80	4.96	330.7	4.69		
60	19.85	5.05	336.7	4.78		
75	24.89	5.04	336.0	4.77		
90	29.94	5.05	336.7	4.78		
105	34.94	5.00	333.3	4.77		
120	39.95	5.01	334.0	4.74		
135	44.82	4.87	324.7	4.61		
150	49.70	4.88	325.3	4.62		
165	54.50	4.80	320.0	4.54		
180	59.46	4.96	330.7	4.69		
195	64.25	4.79	319.3	4.53		

Run No. 2

15	4.71	4.71	314.0	4.46	23.9	721.3
30	9.60	4.89	326.0	4.63		mm Hg
45	14.49	4.89	326.0	4.63		
60	19.47	4.98	332.0	4.71		
75	24.70	5.23	348.7	4.95		
90	29.68	4.98	332.0	4.71		
105	34.57	4.89	326.0	4.63		
120	39.46	4.89	326.0	4.63		
135	44.43	4.97	331.3	4.70		
150	49.32	4.89	326.0	4.63		
165	54.13	4.81	320.7	4.55		
180	59.01	4.88	325.3	4.62		

Average maximum rate for Run No. 1: 329.49 mm^3/cm^2-min., and 4.679 mg/cm^2-min.

Average maximum rate for Run No. 2: 329.09 mm^3/cm^2-min., and 4.672 mg/cm^2-min.

Table XIX Continued

Average maximum rate for both runs: 329.29 mm^3/cm^2-min., and 4.675 mg/cm^2-min.

Table XX

The rate of dissolution of Ti in 4N H_2SO_4 plus 1N NH_4F

Run No. 1

Time (Min.)	Volume H_2 (c.c.)	Volume (c.c.)	Rate (mm^3/cm^2-min.)	Rate (mg/cm^2-min.)	Temp °C (Avg.)	Pressure Corrected
10	4.75	4.75	475	6.74	25.9	706.7
20	9.68	4.93	493	7.00		mm Hg
30	14.69	5.01	501	7.11		
40	19.70	5.01	501	7.11		
50	24.96	5.26	526	7.47		
60	30.05	5.09	509	7.23		
70	34.89	4.84	484	6.87		
80	39.73	4.84	484	6.87		
90	44.83	5.10	510	7.24		
100	49.67	4.84	484	6.87		
110	54.76	5.09	509	7.23		
120	59.60	4.84	484	6.87		
130	64.44	4.84	484	6.87		
140	69.45	5.01	501	7.11		
150	74.29	4.84	484	6.87		

Run No. 2

10	4.74	4.74	474	6.73	23.85	699.72
20	9.49	4.75	475	6.74		mm Hg
30	14.40	4.91	491	6.97		
40	19.31	4.91	491	6.97		
50	24.31	5.00	500	7.10		
60	29.14	4.83	483	6.86		
70	34.13	4.99	499	7.08		
80	39.13	5.00	500	7.10		
90	44.04	4.91	491	6.97		
100	48.96	4.92	492	6.99		
110	54.04	5.08	508	7.21		
120	58.95	4.91	491	6.97		
130	63.86	4.91	491	6.97		
140	68.78	4.92	492	6.97		

Table XX Continued

Average maximum rate for Run No. 1: 496.71 mm^3/cm^2-min., and 7.051 mg/cm^2-min.

Average maximum rate for Run No. 2: 494.08 mm^3/cm^2-min., and 7.015 mg/cm^2-min.

Average maximum rate for both runs: 495.40 mm^3/cm^2-min., and 7.033 mg/cm^2-min.

Table XXI

The rate of dissolution of Ti in 4N H_2SO_4 plus 2N NH_4F

Run No. 1

Time (Min.)	Volume H_2 (c.c.)	Volume (c.c.)	Rate (mm^3/cm^2-min.)	Rate (mg/cm^2-min.)	Temp °C (Avg.)	Pressure Corrected
5	3.73	3.73	746	10.59	24.35	701.3
10	7.62	3.89	778	11.05		mm Hg
15	11.60	3.98	796	11.30		
20	15.67	4.07	814	11.56		
25	19.90	4.23	846	12.01		
30	24.22	4.32	864	12.27		
35	28.54	4.32	864	12.27		
40	32.86	4.32	864	12.27		
45	37.18	4.32	864	12.27		
50	41.67	4.49	898	12.75		
55	45.99	4.32	864	12.27		
60	50.31	4.32	864	12.27		
65	54.63	4.32	864	12.27		
70	59.03	4.40	880	12.50		
75	63.35	4.32	864	12.27		
80	67.93	4.50	916	13.01		
85	72.33	4.40	880	12.50		
90	76.82	4.49	898	12.75		
95	81.31	4.49	898	12.75		

Average maximum rates Run No. 1: 875.20 mm^3/cm^2-min., and 12.429 mg/cm^2-min.

Table XXII

The dissolution of Ti in 4N H_2SO_4 plus 2N NH_4F

Run No. 2

Time (Min.)	Volume H_2 (c.c.)	Volume (c.c.)	Rate (mm^3/cm^2-min.)	Rate (mg/cm^2-min.)	Temp °C (Avg.)	Pressure Corrected
5	3.54	3.54	708	10.05	25.3	700.4
10	7.25	3.71	742	10.54		mm Hg
15	10.96	3.71	742	10.54		
20	14.67	3.71	742	10.54		
25	18.55	3.88	776	11.02		
30	22.34	3.79	758	10.76		
35	26.22	3.88	776	11.02		
40	30.01	3.79	758	10.76		
45	33.89	3.88	776	11.02		
50	37.60	3.71	742	10.54		
55	41.47	3.87	774	10.99		
60	45.27	3.80	760	10.79		
65	49.06	3.79	758	10.76		
70	52.94	3.88	776	11.02		
75	56.82	3.88	776	11.02		
80	60.78	3.96	792	11.25		
85	64.66	3.88	776	11.02		
90	68.54	3.88	776	11.02		
95	72.33	3.79	758	10.76		
100	76.04	3.71	742	10.54		
105	79.92	3.88	776	11.02		

Average maximum rates Run No. 2: 763.80 mm^3/cm^2-min., and 10.846 mg/cm^2-min.

Average maximum rates for both runs: 819.5 mm^3/cm^2-min., and 11.637 mg/cm^2-min.

(V) Conclusions:

From the results obtained it is evident the stronger the acid mixture was in hydrofluoric acid, formed from ammonium fluoride according to reaction (2), the greater was the rate of dissolution. Although the rate lagged behind that of pure HF, and lost ground steadily above concentrations of 0.5N NH_4F, at which point was the closest agreement for the dissolution rate curves of pure HF, and HF formed from NH_4F in 4N H_2SO_4 solution. As would be expected, the rates of dissolution were much greater than could be expected for titanium in sulphuric acid alone.

PART II

SECTION C

The Rate of Dissolution of Titanium in Varying Concentrations of Hydrochloric Acid, With the Addition of a Constant Amount of Ammonium Fluoride.

As in the similar investigation conducted with sulphuric acid, the investigation of the rate of dissolution of the titanium was based entirely on the collection and measurement of the hydrogen gas evolved.

(i) Method and Apparatus:

The method of procedure and apparatus used in this investigation was the same as that used previously in SECTIONS A and B.

(ii) Procedure:

The procedure used was similar to that employed with sulphuric acid, and tests were also made in this case, to show the dissolution of the titanium continued after the hydrofluoric acid formed from the ammonium fluoride added was exhausted, and that this continued dissolution was due to the hydrochloric acid.

Four different concentrations of hydrochloric acid were used, 0.5N, 2N, 6N and 10N; to each of these 0.1855 grams of ammonium fluoride was added. This was the amount of ammonium fluoride to make the 100 c.c. of solution 1/20N with respect to HF. Assuming that it is possible for the reaction

$$NH_4F + HCl \rightleftharpoons (NH_4)Cl + HF \quad (5)$$

to go to completion so that definite calculations can be made. actually though, this reaction only comes to equilibrium, as in the case of NH_4F added to H_2SO_4 in Reaction (2).

(iii) Results:

It was seen on plotting the average maximum dissolution rates against the concentrations of the normalities, as shown in Figure 5, that the rate of dissolution increased in almost a straight line above 2N HCl, while below 2N the line was curved, with the rate dropping off more rapidly as the concentration of HCl decreased. All these rates for HCl are nearly double the rates found for similar tests with H_2SO_4. From the rates of dissolution given in Tables XXIII to XXVII, it was noticed that the maximum dissolution rate was reached quickly, in all cases, then decreased fairly rapidly from there. After dissolution all the sample surfaces had a dull grey, pebbley finish.

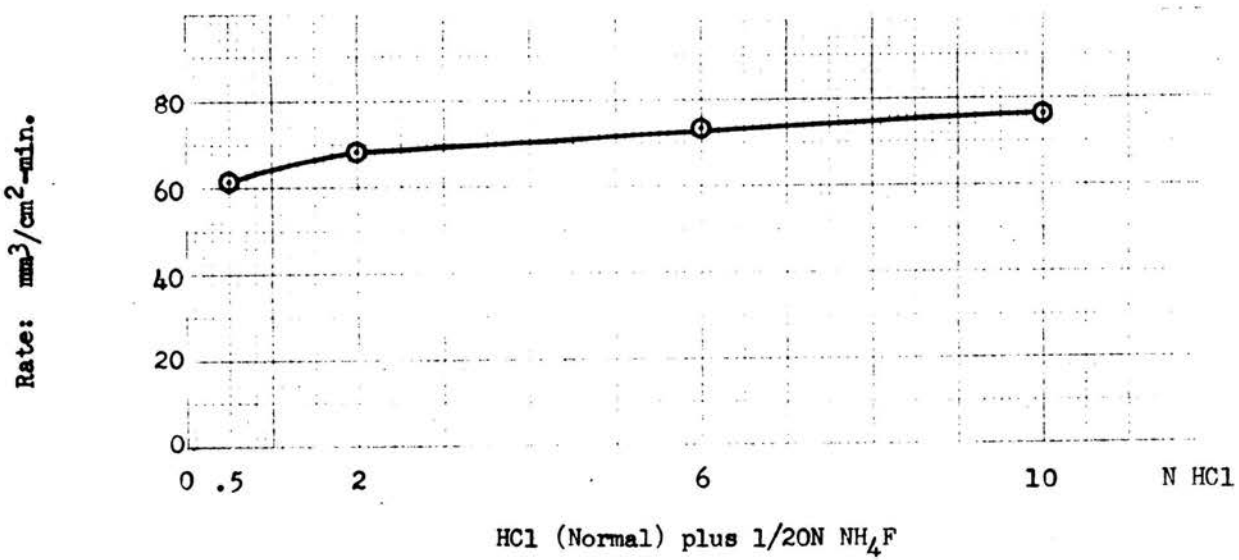

Figure 5

Rate of dissolution of titanium in different concentrations of HCl plus a constant amount of NH_4F.

Table XXIII

Rate of dissolution of Ti in 0.5N HCl plus 1/20 N NH_4F

Run No. 1

Time (Min.)	Volume H_2 (c.c.)	Volume (c.c.)	Rate (mm^3/cm^2-min.)	Rate (mg/cm^2-min.)	Temp °C (Avg.)	Pressure Corrected
20	1.64	1.64	82.0	1.16	23.6	714.3
40	3.03	1.39	69.5	.99		mm Hg
60	4.37	1.34	67.0	.95		
80	5.71	1.34	67.0	.95		
100	6.96	1.25	62.5	.89		
120	8.42	1.46	73.0	1.04		
140	9.86	1.44	72.0	1.02		
160	11.07	1.21	60.5	.86		
180	12.28	1.21	60.5	.86		
200	13.50	1.22	61.0	.87		

Run No. 2

20	1.47	1.47	73.5	1.04	22.5	712.8
40	2.60	1.13	56.5	.80		mm Hg
60	3.68	1.08	54.0	.77		
80	4.67	.99	49.5	.70		
100	5.71	1.04	52.0	.74		
120	6.75	1.04	52.0	.74		
140	7.62	.87	43.5	.62		
160	8.55	.93	46.5	.66		
180	9.48	.93	46.5	.66		
200	10.03	.82	41.0	.58		

Average maximum rates for Run No. 1: 68.22 mm^3/cm^2-min., and 0.969 mg/cm^2-min.

Average maximum rates for Run No. 2: 52.66 mm^3/cm^2-min., and 0.748 mg/cm^2-min.

Average maximum rates for both runs: 60.44 mm^3/cm^2-min., and 0.858 mg/cm^2-min.

Table XXIV

Rate of dissolution of Ti in 2N HCl plus 1/20N NH_4F

Run No. 1

Time (Min.)	Volume H_2 (c.c.)	Volume (c.c.)	Rate (mm^3/cm^2-min.)	Rate (mg/cm^2-min.)	Temp °C (Avg.)	Corrected Pressure
20	1.59	1.59	79.4	1.13	25.1	696.57
40	3.19	1.60	80.0	1.14		mm Hg
60	4.53	1.34	67.0	.95		
80	5.87	1.34	67.0	.95		
100	7.29	1.42	71.0	1.01		
120	8.64	1.35	67.5	.96		
140	10.06	1.42	71.0	1.01		
160	11.32	1.26	63.0	.89		
180	12.58	1.26	63.0	.89		
200	13.83	1.25	62.5	.89		
220	15.09	1.26	63.0	.89		
240	16.35	1.26	63.0	.89		
260	17.61	1.26	63.0	.89		
280	18.87	1.26	63.0	.89		
1170	0	0	0	0		
1190	0.84	0.84	42.0	.60		
1210	1.55	0.71	35.5	.50		
1230	2.26	0.71	35.5	.50		
1250	2.93	0.67	33.5	.48		
	65.63 c.c. H_2					

Average maximum rates for run No. 1: 69.14 mm^3/cm^2-min., and 0.982 mg/cm^2-min.

Table XXV

Rate of dissolution of Ti in 2N HCl plus 1/20N NH_4F

Run No. 2

Time (Min.)	Volume H_2 $(c.c.)^2$	Volume (c.c.)	Rate (mm^3/cm^2-min.)	Rate (mg/cm^2-min.)	Temp °C (Avg.)	Corrected Pressure
20	1.53	1.53	76.5	1.09	24.3	703.41
40	2.97	1.44	72.0	1.02		mm Hg
60	4.42	1.45	72.5	1.03		
80	5.86	1.44	72.0	1.02		
100	7.31	1.45	72.5	1.03		
120	8.75	1.44	72.0	1.02		
140	10.03	1.28	64.0	.91		
160	11.30	1.27	63.5	.90		
180	12.58	1.28	64.0	.91		
200	13.68	1.10	55.0	.78		
220	14.79	1.11	55.5	.79		
240	15.89	1.10	55.0	.78		
260	17.12	1.23	61.5	.87		
280	18.36	1.24	62.0	.88		
300	19.46	1.10	55.0	.78		
320	20.57	1.11	55.5	.79		
1160	0	0	0	0		
1180	.85	.85	42.5	.60		
1200	1.53	.68	34.0	.48		
1220	2.21	.68	34.0	.48		
1240	2.89	.68	34.0	.48		
	61.03 c.c. H_2					

Average maximum rates for run No. 2: 67.22 mm^3/cm^2-min., and 0.954 mg/cm^2-min.

Average maximum rates for both runs: 68.18 mm^3/cm^2-min., and 0.968 mg/cm^2-min.

Table XXVI

Rate of dissolution of Ti in 6N HCl plus 1/20N NH_4F

Run No. 1

Time (Min.)	Volume H_2 (c.c.)	Volume (c.c.)	Rate (mm^3/cm^2-min.)	Rate (mg/cm^2-min.)	Temp °C (Avg.)	Corrected Pressure
20	1.30	1.30	65.0	.92	23.1	716.07
40	3.00	1.70	85.0	1.21		mm Hg
60	4.60	1.60	80.0	1.14		
80	6.08	1.48	74.0	1.05		
100	7.56	1.48	74.0	1.05		
120	8.90	1.34	67.0	.95		
140	10.25	1.35	67.5	.96		
160	11.47	1.22	61.0	.87		
180	12.68	1.21	60.5	.87		
200	13.81	1.13	56.5	.80		

Run No. 2

20	1.47	1.47	73.5	1.04	22.5	711.20
40	2.94	1.47	73.5	1.04		mm Hg
60	4.41	1.47	73.5	1.04		
80	5.88	1.47	73.5	1.04		
100	7.26	1.38	69.0	.98		
120	8.78	1.52	76.0	1.08		
140	10.29	1.51	75.5	1.07		
160	11.76	1.47	73.5	1.04		
180	13.14	1.38	69.0	.98		
200	14.52	1.38	69.0	.98		

Average maximum rates for run No. 1: 70.44 mm^3/cm^2-min., and 1.002 mg/cm^2-min.

Average maximum rates for run No. 2: 73.00 mm^3/cm^2-min., and 1.234 mg/cm^2-min.

Average maximum rates for both runs: 71.72 mm^3/cm^2-min., and 1.018 mg/cm^2-min.

Table XXVII

Rate of dissolution of Ti in 10N HCl plus 1/20N NH_4F

Run No. 1

Time (Min.)	Volume H_2 (c.c.)	Volume (c.c.)	Rate (mm^3/cm^2-min.)	Rate (mg/cm^2-min.)	Temp °C (Avg.)	Corrected Pressure
20	1.91	1.91	95.5	1.36	22.7	716.6
40	3.74	1.83	91.5	1.30		mm Hg
60	5.66	1.92	96.0	1.36		
80	7.49	1.83	91.5	1.30		
100	9.23	1.74	87.0	1.23		
120	10.97	1.74	87.0	1.23		
140	12.71	1.74	87.0	1.23		
160	14.32	1.61	80.5	1.14		
180	15.93	1.61	80.5	1.14		
200	17.50	1.57	78.5	1.11		
220	19.15	1.65	82.5	1.17		
240	20.72	1.57	78.5	1.11		
260	22.28	1.56	78.0	1.09		

Run No. 2

20	1.56	1.56	78.0	1.11	23.5	714.25
40	2.94	1.38	69.0	.98		mm Hg
60	4.15	1.21	60.5	.86		
80	5.36	1.21	60.5	.86		
100	6.75	1.39	69.5	.99		
120	8.07	1.32	66.0	.94		
140	9.39	1.32	66.0	.94		
160	10.72	1.33	66.5	.94		
180	11.94	1.22	61.0	.87		
200	13.15	1.21	60.5	.86		
220	14.41	1.26	63.0	.89		
240	15.66	1.25	62.5	.89		
260	16.79	1.13	56.5	.80		

Table XXVII Continued

Average maximum rates for Run No. 1: 86.33 mm^3/cm^2-min., and 1.223 mg/cm^2-min.

Average maximum rates for Run No. 2: 65.25 mm^3/cm^2-min., and 0.927 mg/cm^2-min.

Average maximum rates for both runs: 75.79 mm^3/cm^2-min., and 1.075 mg/cm^2-min.

(iv) Conclusions:

It was shown that hydrochloric acid reacts with titanium on a slowly increasing ratio between the rate of dissolution of the titanium and the increasing concentration of the hydrochloric acid. Below concentration of 2N HCl + NH_4F the rate of increase is more rapid than with concentrations above 2N HCl + NH_4F. The former being a curve, and the latter a straight line ratio. The equation for the straight line ratio is $y-1.56x-69.16=0$, and the slope is $\frac{4.07}{4}$. This slope is quite close to the slope of $\frac{4.52}{4}$ found for the straight line relationship of H_2SO_4 plus NH_4F. The ammonium fluoride added to the hydrochloric acid, and forming HF, permitted the titanium to be much more readily attacked than by HCl alone. Previous investigations 5) had

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5) Straumanis, M. E., and Chen, P. C., The Corrosion of Titanium in Acids, Corrosion Z, 7, 229-237, (1951)

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shown titanium to be unattacked by 1N HCl at room temperature, as compared with a rate of dissolution of 63 mm^3/cm^2-min. in 1N HCl plus NH_4F at 25° C.

PART II

SECTION D

The Rate of Dissolution of Titanium in a Constant Concentration of Hydrochloric Acid, With the Addition of Varying Amounts of Ammonium Fluoride.

As in the three previous SECTIONS A, B and C, the rate of dissolution of titanium was based solely on the collection and measurement of the hydrogen gas evolved. The method of procedure and apparatus was similar to that used and described in SECTION A.

(i) Methods and Procedure:

Six different concentrations of ammonium fluoride were added to 2N HCl. The amounts of NH_4F being 0.1855, 0.371, 0.742, 1.855, 2.78 and 3.71 grams, to give respectively 1/20, 1/10, 1/5, 1/2, 3/4 and 1N strengths with respect to hydrofluoric acid in 100 c.c. of solution. Assuming, in this case also, it is possible for the reaction

$$NH_4F + HCl \rightleftarrows (NH_4)Cl + HF \qquad (5)$$

to go to completion.

(ii) Results:

It was seen on plotting the average maximum dissolution rates against the concentrations of hydrofluoric acid formed on adding ammonium fluoride to 2N HCl, as shown in Figure 6, the rate of dissolution increased with increased amounts of NH_4F. However the rate of increase

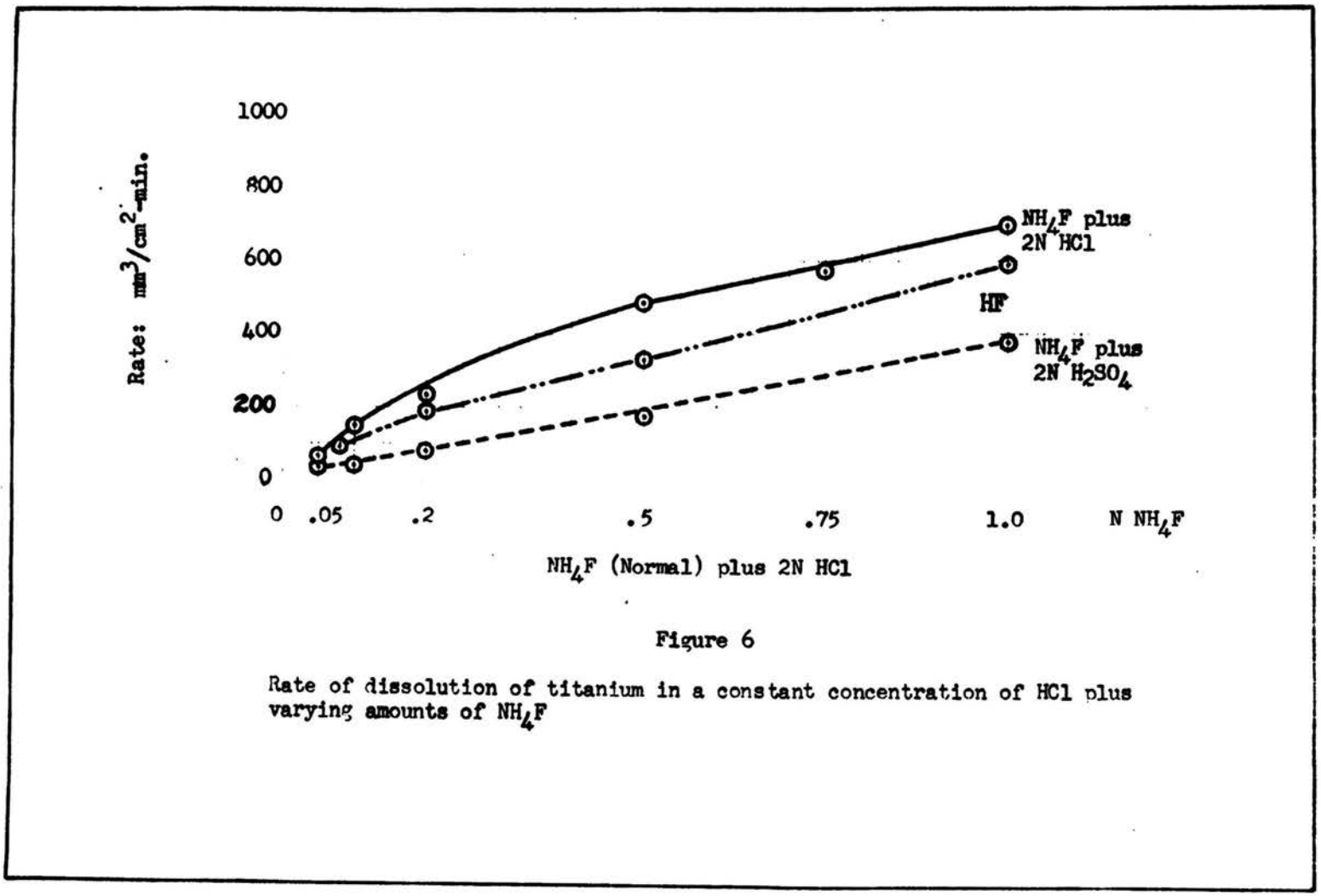

Figure 6

Rate of dissolution of titanium in a constant concentration of HCl plus varying amounts of NH_4F

was greatest with the smaller additions of NH_4F, then began to flatten out somewhat with larger additions of NH_4F. As was found in the similar investigation when NH_4F was added to H_2SO_4, plotting the rate of dissolution against amounts of NH_4F added to 2N HCl gave a straight line relationship above concentrations of 0.5N HF, formed from the NH_4F, and a curved line below 0.5N HF. The dissolution rate was greater in 2N HCl NH_4F than it was in 2N H_2SO_4 NH_4F, (results for 2N H_2SO_4 plus NH_4F from SECTION F) both having NH_4F added in increasing amounts, or in HF alone. From the rates of dissolution given in Tables XXVIII to XXXIII, it is seen that the maximum rate of dissolution needed a short induction period in concentrations above 1/2N with respect to HF, but below that concentration the maximum rate was achieved almost immediately. In all cases the maximum rate was sustained for a considerable time before gradually dropping off. In each instance the titanium sample surface was dull and rough after dissolution.

Table XXVIII

The rate of dissolution of Ti in 2N HCl plus 1/20 N NH_4F

Run No. 1

Time (Min.)	Volume H_2 (c.c.)	Volume (c.c.)	Rate (mm^3/cm^2-min.)	Rate (mg/cm^2-min.)	Temp °C (Avg.)	Corrected Pressure
20	1.59	1.59	79.4	1.13	25.1	696.57
40	3.19	1.60	80.0	1.14		mm Hg
60	4.53	1.34	67.0	.95		
80	5.87	1.34	67.0	.95		
100	7.29	1.42	71.0	1.01		
120	8.64	1.35	67.5	.96		
140	10.06	1.42	71.0	1.01		
160	11.32	1.26	63.0	.89		
180	12.58	1.26	63.0	.89		
200	13.83	1.25	62.5	.89		
220	15.09	1.26	63.0	.89		

Run No. 2

20	1.53	1.53	76.5	1.09	24.3	703.41
40	2.97	1.44	72.0	1.02		mm Hg
60	4.42	1.45	72.5	1.03		
80	5.86	1.44	72.0	1.02		
100	7.31	1.45	72.5	1.03		
120	8.75	1.44	72.0	1.02		
140	10.03	1.28	64.0	.91		
160	11.30	1.27	63.5	.90		
180	12.58	1.28	64.0	.91		
200	13.68	1.10	55.0	.78		
220	14.79	1.11	55.5	.79		
240	15.89	1.10	55.0	.78		

Average maximum rates for Run No. 1: 69.14 mm^3/cm^2-min., and 0.982 mg/cm^2-min.

Average maximum rates for Run No. 2: 67.22 mm^3/cm^2-min., and 0.954 mg/cm^2-min.

Average maximum rates for both runs: 68.18 mm^3/cm^2-min., and 0.968 mg/cm^2-min.

Table XXIX

The rate of dissolution of Ti in 2N HCl plus 1/10N NH_4F

Run No. 1

Time (Min.)	Volume H_2 (c.c.)	Volume (c.c.)	Rate (mm^3/cm^2-min.)	Rate (mg/cm^2-min.)	Temp °C (Avg.)	Corrected Pressure
10	1.55	1.55	1.55	2.20	23.3	709.3
20	3.10	1.55	1.55	2.20		mm Hg
30	4.81	1.71	1.71	2.43		
40	6.28	1.47	1.47	2.09		
50	7.74	1.46	1.46	2.07		
60	9.29	1.55	1.55	2.20		
70	10.75	1.46	1.46	2.07		
80	12.12	1.37	1.37	1.94		
90	13.54	1.42	1.42	2.02		
100	14.96	1.42	1.42	2.02		
110	16.51	1.55	1.55	2.20		
120	17.89	1.38	1.38	1.96		
130	19.35	1.46	1.46	2.07		
140	20.81	1.46	1.46	2.07		
150	22.27	1.46	1.46	2.07		

Run No. 2

10	1.57	1.57	157	2.23	22.5	717.6
20	3.14	1.57	157	2.23		mm Hg
30	4.71	1.57	157	2.23		
40	6.28	1.57	157	2.23		
50	7.85	1.57	157	2.23		
60	9.33	1.48	148	2.10		
70	10.82	1.49	149	2.12		
80	12.30	1.48	148	2.10		
90	13.70	1.40	140	1.99		
100	15.26	1.56	156	2.21		
110	16.66	1.40	140	1.99		
120	18.06	1.40	140	1.99		
130	19.54	1.48	148	2.10		
140	20.85	1.31	131	1.86		

Table XXIX Continued

Average maximum rates for Run No. 1: 148.64 mm^3/cm^2-min., and 2.110 mg/cm^2-min.

Average maximum rates for Run No. 2: 150.31 mm^3/cm^2-min., and 2.135 mg/cm^2-min.

Average maximum rates for both runs: 149.48 mm^3/cm^2-min., and 2.123 mg/cm^2-min.

Table XXX

The rate of dissolution of Ti in 2N HCl plus 1/5N NH_4F

Run No. 1

Time (Min.)	Volume H_2 (c.c.)	Volume (c.c.)	Rate (mm^3/cm^2-min.)	Rate (mg/cm^2-min.)	Temp °C (Avg.)	Corrected Pressure
10	2.27	2.27	227	3.22	21.6	715.9
20	4.54	2.27	227	3.22		mm Hg
30	6.81	2.27	227	3.22		
40	9.08	2.27	227	3.22		
50	11.35	2.27	227	3.22		
60	13.62	2.27	227	3.22		
70	15.89	2.27	227	3.22		
80	18.07	2.18	218	3.10		
90	20.30	2.23	223	3.17		
100	22.52	2.22	222	3.15		
110	24.79	2.27	222	3.22		
120	27.06	2.27	227	3.22		

Run No. 2

10	2.36	2.36	236	3.35	21.7	718.72
20	5.08	2.72	272	3.86		mm Hg
30	7.62	2.54	254	3.61		
40	10.16	2.54	254	3.61		
50	12.79	2.63	263	3.73		
60	15.42	2.63	263	3.73		
70	17.93	2.51	251	3.56		
80	20.45	2.52	252	3.58		
90	22.95	2.50	250	3.55		
100	25.32	2.37	237	3.36		
110	27.86	2.54	254	3.61		
120	30.40	2.54	254	3.61		
130	32.85	2.45	245	3.48		
140	35.30	2.45	245	3.48		
150	37.76	2.46	246	3.49		
160	40.21	2.45	245	3.48		

Table XXX Continued

Average maximum rates for Run No. 1: 225.5 mm^3/cm^2-min., and 3.20 mg/cm^2-min.

Average maximum rates for Run No. 2: 252.33 mm^3/cm^2-min., and 3.583 mg/cm^2-min.

Average maximum rates for both runs: 238.91 mm^3/cm^2-min., and 3.391 mg/cm^2-min.

Table XXXI

The Rate of dissolution of Ti in 2N HCl plus 1/2N NH_4F

Run No. 1

Time (Min.)	Volume H_2 (c.c.)	Volume (c.c.)	Rate (mm^3/cm^2-min.)	Rate (mg/cm^2-min.)	Temp °C (Avg.)	Corrected Pressure
10	4.78	4.78	478	6.79	26.2	710.79
20	9.72	4.94	494	7.01		mm Hg
30	14.84	5.12	512	7.27		
40	19.87	5.03	503	7.14		
50	24.91	5.04	504	7.16		
60	30.20	5.29	529	7.51		
70	35.31	5.11	511	7.26		
80	40.35	5.04	504	7.16		
90	45.38	5.03	503	7.14		
100	50.33	4.95	495	7.03		
110	55.27	4.94	494	7.01		
120	60.22	4.95	495	7.03		
130	65.34	5.12	512	7.27		

Run No. 2

10	4.51	4.51	451	6.40	24.3	717.91
20	9.28	4.77	477	6.77		mm Hg
30	14.13	4.85	485	6.89		
40	18.81	4.68	468	6.65		
50	23.58	4.77	477	6.77		
60	28.26	4.68	468	6.65		
70	32.86	4.60	460	6.53		
80	37.45	4.59	459	6.52		
90	42.14	4.69	469	6.66		
100	46.64	4.50	450	6.39		
110	51.15	4.51	451	6.40		
120	55.66	4.51	451	6.40		

Table XXXI Continued

Average maximum rates for Run No. 1: 504.67 mm^3/cm^2-min., and 7.166 mg/cm^2-min.

Average maximum rates for Run No. 2: 463.86 mm^3/cm^2-min., and 6.585 mg/cm^2-min.

Average maximum rates for both runs: 484.25 mm^3/cm^2-min, and 6.875 mg/cm^2-min.

Table XXXII

The rate of dissolution of Ti in 2N HCl plus 3/4N NH_4F

Run No. 1

Time (Min.)	Volume H_2 (c.c.)	Volume (c.c.)	Rate (mm^3/cm^2-min.)	Rate (mg/cm^2-min.)	Temp °C (Avg.)	Corrected Pressure
5	2.94	2.94	588	8.35	22.9	713.34
10	6.06	3.12	624	8.86		mm Hg
15	9.18	3.12	624	8.86		
20	12.21	3.03	606	8.60		
25	15.15	2.94	588	8.35		
30	18.10	2.95	590	8.38		
35	21.04	2.94	588	8.35		
40	23.90	2.86	572	8.12		
45	26.93	3.03	606	8.60		
50	29.79	2.86	572	8.12		
55	32.73	2.94	588	8.35		
60	35.68	2.95	590	8.38		
65	38.62	2.94	588	8.35		
70	41.74	3.12	624	8.86		

Run No. 2

5	2.41	2.41	482	6.84	23.55	712.0
10	5.17	2.76	552	7.84		mm Hg
15	8.11	2.94	588	8.35		
20	10.87	2.76	552	7.84		
25	13.54	2.67	534	7.58		
30	16.39	2.85	570	8.09		
35	19.14	2.75	550	7.81		
40	22.08	2.94	588	8.35		
45	24.84	2.76	552	7.84		
50	27.60	2.76	552	7.84		
55	30.37	3.77	554	7.87		
60	33.12	2.75	550	7.81		
65	35.88	2.76	552	7.84		

Table XXXII Continued

Average maximum rate for Run No. 1: 596.29 mm^3/cm^2-min., and 8.466 mg/cm^2-min.

Average maximum rate for Run No. 2: 557.83 mm^3/cm^2-min., and 7.922 mg/cm^2-min.

Average maximum rate for both runs: 577.06 mm^3/cm^2-min., and 8.194 mg/cm^2-min.

Table XXXIII

The rate of dissolution of Ti in 2N HCl plus 1N NH_4F

Run No. 1

Time (Min.)	Volume H_2 (c.c.)	Volume (c.c.)	Rate (mm^3/cm^2-min.)	Rate (mg/cm^2-min.)	Temp °C (Avg.)	Corrected Pressure
10	5.88	5.88	588	8.35	21.9	710.09
15	9.34	3.46	692	9.83		mm Hg
20	12.80	3.46	692	9.83		
25	16.35	3.55	710	10.08		
30	19.89	3.54	708	10.05		
35	23.44	3.55	710	10.08		
40	27.07	3.63	726	10.31		
45	30.88	3.81	762	10.82		
50	34.68	3.80	760	10.79		
55	38.23	3.55	710	10.08		
60	41.69	3.46	692	9.83		

Run No. 2

5	3.28	3.28	656	9.31	22.4	709.51
10	6.64	3.36	672	9.54		mm Hg
15	10.01	3.37	674	9.57		
20	13.46	3.45	690	9.80		
25	16.74	3.28	656	9.31		
30	20.19	3.45	690	9.80		
35	23.47	3.28	656	8.31		
40	26.83	3.36	672	9.54		
45	30.20	3.37	674	9.57		
50	33.48	3.28	656	9.31		

Average maximum rates for Run No. 1: 718.88 mm^3/cm^2-min., and 10.21 mg/cm^2-min.

Average maximum rates for Run No. 2: 669.60 mm^3/cm^2-min., and 9.506 mg/cm^2-min.

Average maximum rates for both runs: 694.24 mm^3/cm^2-min., and 9.858 mg/cm^2-min.

(iii) Conclusions:

From the results obtained it is evident the stronger the acid mixture was in hydrofluoric acid, formed from the ammonium fluoride, the greater was the rate of dissolution. The rate of dissolution increased more rapidly with concentrations of NH_4F up to 0.5N, then gradually tapered off, although still increasing. The rates of dissolution were much greater than for titanium in hydrochloric acid alone, as HCl by itself does not attack titanium at room temperatures in concentrations below 2N HCl according to Straumanis and Chen. [5] The slope of the straight line relationship between the rate of dissolution and concentration of 2N HCl plus NH_4F (Normal) above 0.5N was $\frac{200}{.4}$, and for the

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5) Straumanis, M. E., and Chen, P. C., The Corrosion of Titanium in Acids, Corrosion Z, 7, 229-237, (1951)

---

similar relationship with $2H_2SO_4 + NH_4F$ the slope was also $\frac{200}{.4}$.

The fact that the rate of dissolution of titanium in 2N HCl plus NH_4F was found to be somewhat greater than the rate of dissolution in HF alone may have several explanations. One is that HCl is a strong acid, and being such it is possible that the reaction

$$NH_4F + HCl \rightleftharpoons (NH_4)Cl + HF \qquad (5)$$

goes very nearly to completion; much more so than in the case of NH_4F added to a weaker acid H_2SO_4. The values for the rate of dissolution

of Ti in HF were taken from a work by Straumanis and Chen [2], and

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2) Straumanis, M. E. and Chen, P. C., op. cit. p. 239

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their data with the data from this investigation on the rate of dissolution of Ti in HCl plus NH_4F, both being within their respective experimental error limits, could give such a discrepancy. Then, it might be possible that the variation in rates of dissolution was due to some unanticipated secondary reaction which cannot be explained.

PART II

SECTION E

The Effect of Addition Agents on the Rate of Dissolution of a Titanium Electrode in 1N HF.

(i) Method, Apparatus and Procedure:

The rate of dissolution was computed solely from the amount of H_2 evolved, and the method, apparatus and procedure was similar to that described in previous tests made on rates of dissolution. The one innovation being the addition agent was not added until the dissolution rate of Ti in 1N HF alone had passed its maximum. The addition agents were dilute $PtCl_4$, 10 c.c. 2% agar-agar, and 2 c.c. 2% agar-agar solutions.

(ii) Results:

The results obtained are given in Tables XXXIV to XXXVI, and show that the rate of dissolution increased greatly with additions of $PtCl_4$ while it decreased with additions of Agar-Agar. The percentage of rate of increase with the $PtCl_4$ added was 220.5%, and the percentage decrease of rate was 17.2% with 10 c.c. 2% agar-agar, and 5.32% with 2 c.c. 2% agar-agar.

Table XXXIV

The rate of dissolution of Ti in 1N HF plus dilute $PtCl_4$

Time (Min.)	Volume H_2 (c.c.)	Volume (c.c.)	Rate (mm^3/cm^2-min.)	Temp °C (Avg.)	Pressure Corrected
15	6.62	6.62	441.3	21.5	714.62
30	14.21	7.59	506.0		mm Hg
45	21.97	7.76	517.3		
60	29.81	7.84	522.7		
75	37.66	7.85	523.3		
90	45.59	7.93	528.7		
105	53.35	7.76	517.3		
120	61.11	7.76	517.3		
135	68.78	7.67	511.3		
15	24.58	24.58	1638.7	1 c.c. dilute $PtCl_4$ added	
30	47.59	23.01	1534		
40	69.65	22.06	1470.7		
60	90.83	21.18	1412		
75	112.19	21.36	1424		

Percentage of increase in rate of dissolution,

$$\frac{1638.7-511.3}{511.3} \times 100\% = 220.5\% \text{ increase}$$

Table XXXV

The rate of dissolution of Ti in 1N HF plus 10 c.c. 2% Agar-Agar.

Time (Min.)	Volume H_2 (c.c.)	Volume (c.c.)	Rate (mm^3/cm^2-min.)	Temp °C (Avg.)	Pressure Corrected
15	6.31	6.31	420.7	22.0	720.01
30	14.38	8.07	538		mm Hg
45	22.79	8.41	560.7		
60	31.03	8.24	549.7		
75	39.28	8.25	549.7		
90	47.78	8.50	566.7		
105	56.11	8.33	555.3		
120	64.0	7.89	526		
135	71.89	7.89	526		
150	80.39	8.50	566.7		
165	88.72	8.33	555.3		
15	7.01	7.01	467.3	10 c.c., 2% Agar-Agar	
30	13.5	6.49	432.7		
45	20.16	6.66	444		
60	26.65	6.49	432.7		
75	33.31	6.66	444		

Percentage of decrease in rate of dissolution

$$\frac{555.3-467.3}{555.3} \times 100\% = 17.2\% \text{ decrease}$$

Table XXXVI

The rate of dissolution of Ti in 1N HF plus 2 c.c., 2% Agar-Agar

Time (Min.)	Volume H_2 (c.c.)	Volume (c.c.)	Temp °C (Avg.)	Pressure Corrected
15	6.35	6.35	22.0	714.83
30	14.10	7.75		mm Hg
45	22.11	8.01		
60	30.2	8.09		
75	38.21	8.01		
90	46.57	8.36		
105	54.83	8.26		
120	62.93	8.10		
135	71.02	8.09		
150	79.29	8.27		
15	7.83	7.83	2 c.c., 2% Agar-Agar	
30	15.58	7.75		
45	23.15	7.57		
60	30.81	7.66		
75	38.3	7.49		

Percentage of decrease in rate of dissolution

$$\frac{8.27-7.83}{8.27} \times 100\% = 5.32\% \text{ decrease}$$

(iii) Conclusions:

It can be concluded that the $PtCl_4$ was reduced to fine metallic platinum according to the reaction,

$$PtCl_4 + 4TiF_3 \longrightarrow Pt + TiCl_4 + 3TiF_4 \qquad (6)$$

These fine platinum particles partially precipitated on the surface of the Ti forming minute local cathodes with low overvoltage on Ti and consequently accelerating the rate of dissolution.

The agar-agar in solution acted in the reverse manner, coating the minute local cathodes formed by impurities on the Ti and blanketing their effects, to decrease the rate of dissolution (see page 160).

The Effect of Addition Agents on the Potential of a Titanium Electrode in Hydrofluoric Acid.

The apparatus used was similar to that described in Chapter F for the measurement of the potential of a titanium electrode in a beaker in air, and consisted of the titanium electrode, a potentiometer, and an agar-1N KCl bridge with a calomel half cell.

The procedure followed was to read the potential of the titanium electrode in 1N HF alone until a constant potential was reached, then add the addition agent and note any change in potential measurements. The addition agents added were: 0.1M $AuCl_4$, 0.1M $CuSO_4$, 0.1M $NiSO_4$, 0.1M $PbNO_3$, 0.1M $FeSO_4$, 0.1M $Mg(C_2H_3O_2)_3$, and 0.1M $PtCl_4$.

The results obtained from these tests show that there was no change in potential measurements of the titanium electrode after the addition agents were added to the 1N HF electrolyte, except with the Pt Cl_4 where the potential rose to a considerably less negative potential, then dropped back to a steady negative potential less negative than that first recorded in 1N HF alone.

In several instances a dark precipitate was formed after the addition agent was added.

The results for $PtCl_4$ are given in Table XXXVII.

Table XXXVII

The effect of addition agents on the potential of a Ti electrode in 1N HF.

Addition Agent	Potential (Volts) H_2 Scale	Time (Min.)	Remarks
	-.819	0	strong H_2 evolution
	-.819	5	
	-.819	10	
	-.819	15	
0.1 c.c.; 0.1M $PtCl_4$	-.653	0	very strong H_2 evolution
	-.753	5	dark precipitate
	-.775	10	formed
	-.775	15	
	-.775	20	
	-.775	25	

(i) Conclusions:

As titanium trifluoride is reducing in nature, it would be expected in the cases of $AuCl_3$, $CuSO_4$, $Pb(NO_3)_2$ and $PtCl_4$ that the addition agents were reduced to fine metallic particles of the respective metals. As an example, in the case of $PtCl_4$ this reaction would be,

$$PtCl_4 + 4TiF_3 \rightarrow Pt + TiCl_4 + 3TiF_4 \qquad (6)$$

In the solutions where precipitates were formed, the precipitates would be due to sufficient metal particles being in suspension to colour the acid solution and turn it dark. In the case of $NiSO_4$, $FeSO_4$ and $Mg(C_2H_3O_2)_2$ additions, where no precipitates were formed, the Ti itself may have reduced the nickel or iron ions to the metallic state on the surface of the titanium.

Only in the case of $PtCl_4$ additions did the platinum particles that partially pricipitated on the Ti electrode surface, in the manner

$$3Pt^{++++} + 4Ti \rightarrow 4Ti^{+++} + 3Pt(\text{on Ti}) \qquad (7)$$

have any effect on the potential measurements. The potential first rising considerably, then as the platinum particles started to separate from the Ti surface, decreasing the rate of dissolution, the potential dropped again to a constant value.

PART II

SECTION F

Potential Measurements and Dissolution Rates of Titanium in a Constant Concentration of Sulphuric Acid With the Addition of Varying Amounts of Ammonium Fluoride.

The measurement of the potential at the surface of a metal which is actually corroding, and therefore not in equilibrium with the liquid, often gives much information regarding the corrosion process, according to U. R. Evans 4). The procedure followed in the series of

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4) Evans, Ulick R., Metallic Corrosion Passivity and Protection, Longmans, Green and Co., New York, 757, (1948)

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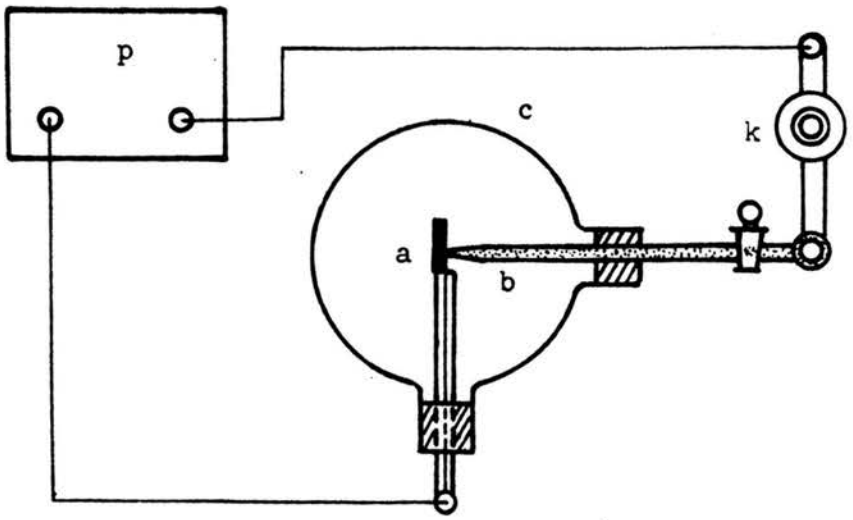
investigations to be described was to run tests of the rate of dissolution with simultaneous potential measurements, and then to attempt a correlation between the two.

(i) Method and Apparatus:

The apparatus for this series of investigations is shown in Figure 7, and included the same thermoregulated water bath, stirring mechanism, and burette to catch the evolved hydrogen gas, as was used to investigate the dissolution rates of titanium in sulphuric and hydrochloric acids with added ammonium fluoride. However, in this case the flask used was slightly different, and was a specially blown, 200 c.c.



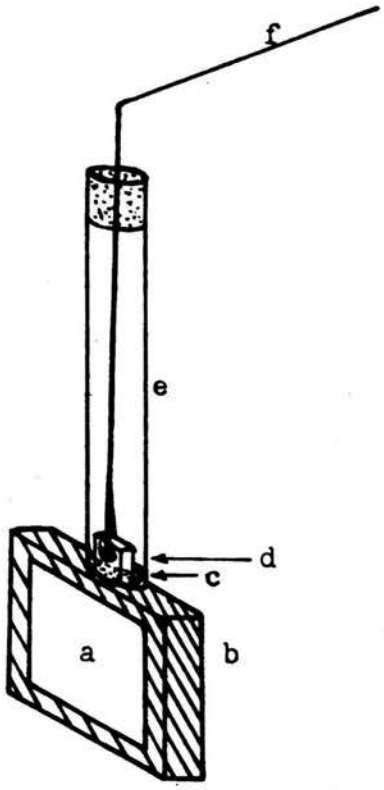
a - Ti electrode
b - capillary tube from calomel cell
c - paraffin lined flask
k - calomel cell
p - potentiometer

Figure 7

Apparatus for potential measurements of Ti electrode. Plan section shown of flask with stirring mechanism removed.

Erlenmeyer flask, coated inside with paraffin wax to resist any attack by hydrofluoric acid. The flask had two side openings, through one of which the titanium electrode could be inserted, and through the other a glass capillary tube which was joined to a half cell. The flask also had a funnel and valve connected to it vertically. When the valve was closed, and the rubber stoppers supporting the titanium electrode and capillary tube were in place, the flask was air tight.

Remington Arms titanium was used for the electrode, and the size was two square centimetres, 1.414 centimetres to a side. The sample was embedded in Bakelite with a titanium surface of 2 sq. cm. exposed. A handle about 1 cm. long and 2 mm. wide was left projecting from one side of the electrode, and out through the Bakelite. A small hole was drilled through the handle near its outer end, and through this a copper lead wire was soldered to give a secure contact. The handle of the electrode was fitted into one end of a short piece of glass tubing bent at right angles, with the copper lead wire passing through and out the other end of the tube. A one holed rubber stopper on the glass tube fitted one of the openings in the side of the Erlenmeyer flask and held the electrode in place inside the flask. The glass tube was bent to project above the water surface of the constant temperature water bath. To protect the junction at the handle of the electrode, "de Khotinsky cement" was used to seal off the lower end of the glass tube. This prevented any acid used during the tests from leaking into the glass tube, attacking the copper lead wire, and destroying the electrical contact.



a - Ti surface
b - bakelite mounting
c - de Khotinsky cement seal
d - connecting joint
e - glass tube
f - copper wire

Figure 8

Titanium electrode used for potential **measurements.**

The 1N calomel half cell used was prepared according to the specifications given by W. G. Palmer [7], and checked against a standard Weston cell also prepared according to Palmer [6]. The potentiometer

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7) Palmer, W. G., Experimental Physical Chemistry, Cambridge University Press, 202-205, 214-215, (1941)

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used was a "Portable Precision Potentiometer" with an internal galvanometer, made by the Rubicon Company of Philadelphia. The potentiometer had two scale ranges, 0 to 3.22 volts and 0 to 0.161 volts.

The set-up for the investigation of potential measurement consisted then of a cell of Ti|acid + NH_4F|1N KCl|1N KCl, Hg_2Cl_2|Hg, and a potentiometer by which the voltage of the cell in question could be measured. Hence, the potential developed between the interface of the Ti metal and the acid solution could be calculated.

To insure a good contact between the Ti surface and the 1N calomel half cell, a glass tube was bent into a flat "U" shape, with one end drawn to a fine open tip, and the other end spread to form a sort of a funnel. Next a solution of 1N KCl containing Agar-Agar was heated until quite fluid, then sucked into the glass tube and allowed to harden into a jelly. The tip of the electrode was kept in a moist atmosphere to prevent the jelly from drying and shrinking excessively away from the tip. The fine tip was pressed against the surface of the titanium so that the Agar-Agar jelly, containing 1N KCl, protruding from it made a contact, and the open end of the calomel half cell,

also containing 1N KCl, was pushed into the jelly at the funnel end of the capillary tube. This made a contact from the Ti sample, through the agar-agar jelly containing 1N KCl, to the calomel half cell. A one holed rubber stopper fitted on the capillary tube held it in place in the Erlenmeyer flask's second opening. Both the glass capillary tube and the glass tube supporting the Ti electrode were coated with paraffin to protect them from attack by hydrofluoric acid.

(ii) Procedure:

First, the standard cell incorporated in the Portable Precision Potentiometer was checked against the standard Weston cell, which in turn had been compared for accuracy with other standard cells, and was found to be satisfactory. Then the whole arrangement--potentiometer, jelly filled capillary tube, and calomel half cell—was checked with a zinc electrode of pure standard zinc in equilibrium with 1M $ZnSO_4$ solution, and also found to be satisfactory on comparing the normal electrode potential obtained with that given in the literature. This test was carried out in the following manner. The zinc electrode was immersed in a solution of 1M $ZnSO_4$ contained in a beaker and exposed to air, and the copper lead wire connected to it attached to the negative pole of the potentiometer. Then the capillary tube tip was pressed against the zinc electrode in the solution, the calomel half cell joined to the capillary tube, and the copper lead wire from the half cell connected to the positive pole of the potentiometer. In effect, a cell of Zn|1M $ZnSO_4$|1N KCl|1N KCl, Hg_2Cl_2|Hg was set up, and the potential

read directly from the potentiometer. The temperature was also recorded so that the potential of the normal calomel cell at this particular temperature could be computed and subtracted to reduce the potential of the zinc to the hydrogen electrode scale, and in all cases the potentials listed are in this standard hydrogen scale.

A few preliminary qualitative tests were made with the same arrangement, but the electrode was titanium and the solution 2N sulphuric acid. It was also necessary to reverse the poles, taking the Ti to the positive pole of the potentiometer, as the Ti was more noble than the calomel half cell. This test was used before each run throughout this whole investigation, as a check on whether the Ti electrode and jelly filled capillary tube were alive and behaving normally.

Next, ammonium fluoride was added to the 2N H_2SO_4 in amounts to make the solution 1/10N, 1/5N, 1/2N and 1N with respect to hydrofluoric acid, and the potential read for each case. These tests were made with a Ti electrode which had been standing in air for 8 to 10 months, and on a Ti electrode with a surface freshly polished with emery paper, with no appreciable difference in potentials being noticed, except with the 2N H_2SO_4 alone. When NH_4F was added, the Ti electrode now became less noble than the calomel half cell, and the leads to the potentiometer had to be reversed so that the Ti was connected to the negative pole and the half cell to the positive pole.

Quantitative tests were now made with simultaneous readings of potential and rate of dissolution, using 2N H_2SO_4 throughout and adding sufficient NH_4F to give solutions respectively 1/20N, 1/10N, 1/5N,

1/2N, 1N, 2N, and 4N with respect to HF, as assumed in equation (2).

Almost the same procedure was followed as was carried out while investigating only the rates of dissolution, and described in SECTION A, but with a few alterations. The electrode was inserted through one of the side openings in the Erlenmeyer flask, and the jelly filled capillary tube through the other opening and manoeuvered so that the tip of the tube pressed firmly against the Ti electrode. The rubber stoppers on both glass tubes held them in the Erlenmeyer openings securely, but to make doubly sure there was no leakage of hydrogen gas here, both rubber stoppers were now coated with paraffin to seal any possible openings. The manner in which the H_2 gas evolved was collected, was similar to that used before. The stirring procedure was somewhat different, in that the Ti electrode remained stationary throughout the test, and an ebonite paddle fitted to the ebonite end of the rotating mechanism revolved in the acid mixture above the electrode, washing the hydrogen formed off the electrode surface and stirring the acid mixture. The 140 c.c. of H_2SO_4 added to the flask was sufficient to completely cover the Ti electrode and capillary tube. A potential reading was taken at this time as a check on whether the electrode and jelly filled capillary tube were reading satisfactorily.

The necessary amount of NH_4F to give the required normality with respect to HF for the particular test being made, in 160 c.c. of solution, was dissolved in 10 c.c. of 4N H_2SO_4, and the total volume brought up to 20 c.c. with distilled water. This took care of the

problem of allowing for contained water in the NH_4F, and also assured the addition being made was 2N H_2SO_4. The total volume of 160 c.c. in the flask immersed the ebonite paddle. The 20 c.c. of 2N H_2SO_4 containing the ammonium fluoride was now poured into the flask, the stopcocks were closed, the rotating mechanism turned on at 200 r.p.m. and simultaneous readings of hydrogen gas evolved, and potential measurements taken at 10 minute intervals.

Three runs were also made using 160 c.c. of pure 0.5N, 2N and 3N HF alone, for a comparison. They were conducted in exactly the same way except the apparatus was first flushed with nitrogen, then the whole 160 c.c. of HF acid added to the flask, the stopcocks closed and the run begun.

(iii) Calculations:

The calculations for the rate of dissolution are the same as were illustrated in SECTION A, on the rate of dissolution of titanium in sulphuric acid.

Corrections to reduce the potential measurements to the hydrogen electrode scale were made according to Miller and Reuther [8], and

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8) Miller, F. and Reuther, H., Zeitschrift für Elektrochemie, 49, 497-9, (1943)

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an example of this correction is as follows.

The potential for the normal calomel cell at 25° C = 0.2807 volts.
The correction factor for temperature given by Miller is,

$$0.2807-0.00028(\text{Temp } ^\circ\text{C}-25)$$

Taking results from Table XL as an example.
Average temperature of run = 21.7° C
Correction to give the potential of the half cell at 21.7° C $= 0.2807-0.00028(21.7-25)$
$= + 0.282$ volts.

In table XXXVI after 200 minutes, the potential recorded = -0.854 volts.
Reducing this to the hydrogen scale $(-0.854 + 0.282)$
$= -0.572$ volts.

Therefore, the actual potential recorded is reduced by the potential of the normal calomel cell to give a potential corrected to the hydrogen electrode scale of potentials at 25° C.

(iv) Results:

The results are given in Table XXXVIII for the preliminary qualitative tests made in air with a Ti electrode in a solution of 2N H_2SO_4, 2N H_2SO_4 with NH_4F added to give 1/10N, 1/5N, 1/2N and 1N solutions with respect to HF. From these results it is readily seen that as the NH_4F is added in increasing amounts, the Ti electrode becomes progressively less noble.

The results of the tests with simultaneous measurements of potential and rate of dissolution are recorded in Tables XXXIX to LI. For every run, the corrected potentials obtained with each different rate of dissolution during the run were averaged, to have an average potential corresponding to a certain rate of dissolution, and these results were plotted in Figure 9. As an example with data taken from Table XXXIX:

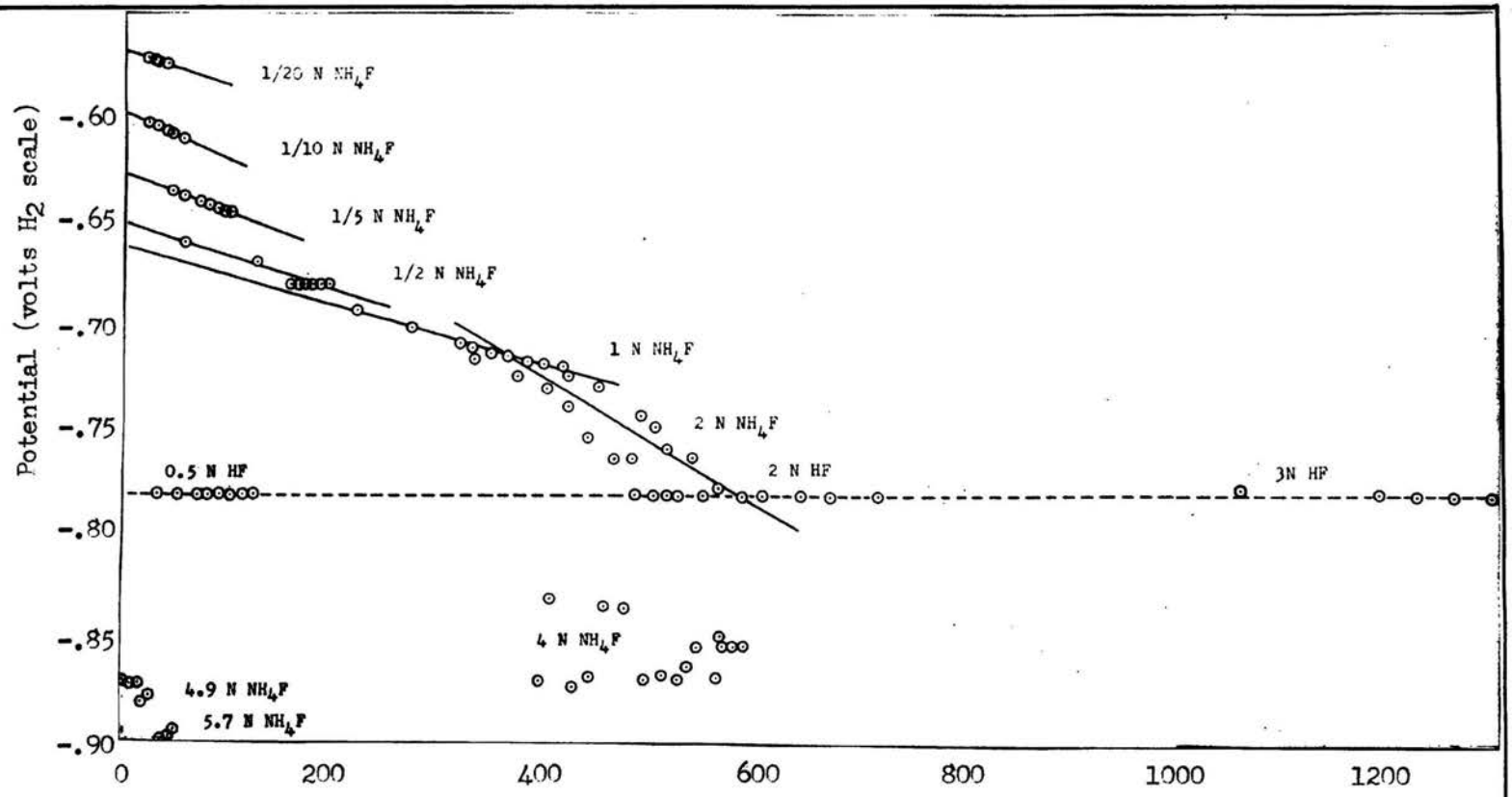

Figure 9

Potential measurements and dissolution rates of Ti electrode in 2N H_2SO_4 plus NH_4F, and pure HF.

Rate of dissolution	21.5 mm^3/cm^2-min.
Potentials at this rate of dissolution	-.856, -.855, -.853, -.854, -.853, -.853, -.852 and -.852 volts
Average potential	-.8522 volts
Potential corrected to H_2 scale at 25° C	-.572 volts

Therefore, the potential corresponding to a dissolution rate of 21.5 mm^3/cm^2-min. is -.572 volts (corrected to H_2 scale).

Two main things are readily seen from Figure 9. Firstly, the potential of the titanium becomes more negative as the amount of NH_4F is increased, and secondly that the potential becomes more negative as the rate of dissolution increases. The runs made in HF alone show that while the rate of dissolution increases with the increasing strength of the hydrofluoric acid, the potential of the Ti electrode is unchanged. With the amount of NH_4F added to 2N H_2SO_4 to give a 4N solution with respect to HF, the results become erratic although the potential still decreases, and the rate of dissolution remains roughly the same as when the amount of NH_4F added gave a 2N solution with respect to HF.

Results were also plotted with still greater concentrations of NH_4F than 4N NH_4F in Figure 9 of potentials and rates of dissolutions in SECTION E, and while the potential continued to become less noble, the rate of dissolution dropped radically, and the results on the whole were quite erratic.

Table XXXVIII

Potential measurements for Ti electrode
Preliminary Qualitative Tests

	Solution	Temp °C	Potential Volts (H_2 Scale)
*	2N H_2SO_4	24.0	+ 0.628
	2N H_2SO_4 1/10N NH_4F	23.8	-0.595
	2N H_2SO_4 1/5N NH_4F	22.0	-0.647
	2N H_2SO_4 1/2N NH_4F	22.0	-0.678
	2N H_2SO_4 1N NH_4F	21.7	-0.718
*	2N H_2SO_4	24.4	+ 0.075
	2N H_2SO_4 1/10N NH_4F	24.3	-0.622
	2N H_2SO_4 1/5N NH_4F	22.8	-0.647
	2N H_2SO_4 1/2N NH_4F	23.0	-0.683
	2N H_2SO_4 1N NH_4F	23.1	-0.717

* Ti electrode had been standing in air for 8-10 months
* Ti electrode freshly polished with emery paper

Table XXXIX

Potential measurements and rate of dissolution of Ti in 2N H_2SO_4 plus 1/20N NH_4F

Time (Min.)	Volume H_2 (c.c.)	Volume (c.c.)	Rate (mm^3/cm^2-min.)	Potential Ti (Volts)	Temp °C (Avg.)	Corrected Pressure
10	1.20	1.2	60.0	- .837	22.0	706.7
20	1.98	.78	39.0	- .849		mm Hg
30	2.75	.77	38.5	- .859		
40	3.44	.69	34.5	- .860		
50	4.22	.78	39.0	- .861		
60	5.03	.81	40.5	- .859		
70	5.85	.82	41.0	- .858		
80	6.54	.69	34.5	- .859		
90	7.23	.69	34.5	- .858		
100	7.83	.60	30.0	- .858		
110	8.52	.69	34.5	- .858		
120	9.12	.60	30.0	- .857		
130	9.64	.52	26.0	- .857		
140	10.15	.51	25.5	- .857		
150	10.58	.43	21.5	- .856		
160	11.01	.43	21.5	- .855		
170	11.53	.52	26.0	- .855		
180	12.05	.52	26.0	- .855		
190	12.56	.51	25.5	- .854		
200	13.08	.52	26.0	- .854		
210	13.51	.43	21.5	- .854		
220	13.94	.43	21.5	- .853		
230	14.46	.52	26.0	- .853		
240	14.89	.43	21.5	- .853		
250	15.40	.51	25.5	- .853		
260	15.83	.43	21.5	- .853		
270	16.26	.43	21.5	- .852		
280	16.69	.43	21.5	- .852		

Average maximum rate of dissolution: 32.70 mm^3/cm^2-min.

Dissolution rate:	21.5	26.0	30.0	34.5	39.0	41.0
Avg. Potential, H_2 scale: corresponding to dissolution rate	.572	.573	.576	.577	.578	.577

Table XL

Potential measurements and rate of dissolution of Ti in 2N H_2SO_4 plus 1/10N NH_4F

Run No. 1

Time (Min.)	Volume H_2 (c.c.)	Volume (c.c.)	Rate (mm^3/cm^2-min.)	Potential Ti (Volts)	Temp °C (Avg.)	Corrected Pressure
10	.69	.69	38.5	- .869	21.7	708.65
20	1.73	1.04	50.2	- .888		mm Hg
30	2.59	.86	43.0	- .890		
40	3.63	1.04	50.2	- .889		
50	4.66	1.03	50.15	- .889		
60	5.61	.95	47.5	- .889		
70	6.65	1.04	50.2	- .889		
80	7.77	1.12	56.0	- .890		
90	8.81	1.04	50.2	- .888		
100	9.85	1.04	50.2	- .889		
110	10.75	.90	45.0	- .887		
120	11.83	1.08	50.4	- .889		
130	12.87	1.04	50.2	- .888		
140	13.91	1.04	50.2	- .888		
150	14.86	.95	47.5	- .888		
160	15.89	1.03	50.15	- .889		
170	16.84	.95	47.5	- .888		
180	17.88	1.04	50.2	- .888		
190	18.83	.95	47.5	- .888		
200	19.86	1.03	50.15	- .887		
210	20.81	.95	47.5	- .887		
220	21.76	.95	47.5	- .887		
230	22.71	.95	47.5	- .888		
240	23.75	1.04	50.2	- .888		
250	24.70	.95	47.5	- .890		
260	25.57	.87	43.5	- .887		

Average maximum rate of dissolution: 48.81 mm^3/cm^2-min.

Dissolution rate:	43.25	45.0	47.5	50.2	50.4	56.0
Avg. corresponding potential, H_2 scale :	.606	.605	.606	.606	.607	.607

Table XLI

Potential measurements and rate of dissolution of Ti in 2N H_2SO_4 plus 1/10N NH_4F

Run No. 2

Time (Min.)	Volume H_2 (c.c.)	Volume (c.c.)	Rate (mm^3/cm^2-min.)	Potential Ti (Volts)	Temp °C (Avg.)	Corrected Pressure
10	.86	.60	30.0	-.888	21.4	705.3
20	1.46	.60	30.0	-.888		mm Hg
30	2.06	.60	30.0	-.887		
40	2.67	.61	30.5	-.886		
50	3.27	.60	30.0	-.886		
60	3.96	.69	34.5	-.886		
70	4.47	.51	25.5	-.886		
80	4.90	.43	21.5	-.885		
90	5.51	.61	30.5	-.886		
100	6.02	.51	25.5	-.885		
110	6.54	.52	26.0	-.885		
120	7.06	.52	26.0	-.885		
130	7.57	.51	25.5	-.885		
140	8.09	.52	26.0	-.884		
150	8.60	.51	25.5	-.884		
160	9.12	.52	26.0	-.884		
170	9.55	.43	21.5	-.884		
180	10.07	.52	26.0	-.884		
190	10.5	.43	21.5	-.884		
200	11.01	.51	25.5	-.884		
210	11.53	.52	26.0	-.884		
220	11.96	.43	21.5	-.884		
230	12.48	.52	26.0	-.883		
240	12.95	.46	23.0	-.884		
250	13.47	.53	26.5	-.883		
260	13.94	.47	23.5	-.883		

Average maximum rate of dissolution: 26.31 mm^3/cm^2-min.
Average maximum rate of dissolution for both runs: 37.56 mm^3/cm^2-min.

Dissolution rate:	21.5	23.0	25.8	30.0	34.5
Avg. corresponding potential, H_2 scale:	-.602	-.6015	-.602	-.605	-.604

Table XLII

Potential measurements and rate of dissolution of Ti in 2N H_2SO_4 plus 1/5N NH_4F

Time (Min.)	Volume H_2 (c.c.)	Volume (c.c.)	Rate (mm^3/cm^2-min.)	Potential (Volts)	Temp °C (Avg.)	Corrected Pressure
10	.90	.90	45.0	- .915	23.05	710.3
20	2.24	1.34	67.0	- .921		mm Hg
30	3.62	1.38	69.0	- .919		
40	5.00	1.38	69.0	- .92		
50	6.38	1.38	69.0	- .92		
60	7.93	1.55	77.5	- .92		
70	9.31	1.38	69.0	- .92		
80	10.73	1.42	71.0	- .919		
90	12.15	1.42	71.0	- .92		
100	13.44	1.29	64.5	- .92		
110	14.65	1.21	60.5	- .918		
120	15.94	1.29	64.5	- .92		
130	17.06	1.12	56.0	- .919		
140	18.27	1.21	60.5	- .918		
150	19.48	1.21	60.5	- .919		
160	20.68	1.20	60.0	- .918		
170	21.80	1.12	56.0	- .918		
180	23.18	1.38	69.0	- .918		
190	24.47	1.29	64.5	- .918		
200	25.85	1.38	69.0	- .918		
210	27.06	1.21	60.5	- .917		
220	28.35	1.29	64.5	- .917		
230	29.65	1.30	65.0	- .917		
240	30.77	1.12	56.0	- .917		
250	31.80	1.03	51.5	- .917		
260	32.92	1.12	56.0	- .916		
270	34.13	1.21	60.5	- .916		
280	35.16	1.03	51.5	- .916		
290	36.28	1.12	56.0	- .917		

Average maximum rate of dissolution: 64.93 mm^3/cm^2-min.

Dissolution rate:	45.0	51.5	56.0	60.5	64.5	67.0	69.0
Avg. corresponding potential, H_2 scale	.634	.6355	.636	.637	.637	.640	.638

	71.0	77.5
continued:	.6385	.639

Table XLIII

Potential measurements and rate of dissolution of Ti in 2N H_2SO_4 plus 1/2N NH_4F

Time (Min.)	Volume H_2 (c.c.)	Volume (c.c.)	Rate (mm^3/cm^2-min.)	Potential (Volts)	Temp °C (Avg.)	Pressure Corrected
10	1.12	1.12	56.0	-.940	23.75	709.75
20	3.69	2.57	128.5	-.954		mm Hg
30	7.04	3.35	167.5	-.957		
40	10.65	3.61	180.5	-.962		
50	14.35	3.70	185.	-.961		
60	18.21	3.86	193.	-.961		
70	22.17	3.96	198.	-.961		
100	29.99			-.961		
110	33.77	3.78	189	-.961		
120	37.55	3.78	189	-.961		
130	41.33	3.78	189	-.961		
140	45.02	3.69	184.5	-.960		
150	48.37	3.35	167.5	-.96		
160	51.47	3.10	155	-.96		
170	54.64	3.17	158.5	-.96		
180	58.25	3.61	180.5	-.96		
190	61.69	3.44	172.	-.96		
200	65.04	3.35	167.5	-.96		
210	68.56	3.52	176	-.96		
220	71.83	3.27	163.5	-.96		
230	75.35	3.52	176	-.96		
240	78.62	3.27	163.5	-.96		

Average maximum rate of dissolution: 176.60 mm^3/cm^2-min.

Dissolution rate:	56.0	128.5	155	158.5	163.5
Avg. corresponding potential, H_2 scale :	-.659	-.673	- .679	-.679	-.679
	167.5	172	176	180.5	185
continued:	-.678	-.679	-.679	-.680	-.680
	189	193	198		
continued:	-.680	-.680	-.680		

Table XLIV

Potential measurements and rate of dissolution of Ti in 2N H_2SO_4 plus 1N NH_4F

Time (Min.)	Volume H_2 (c.c.)	Volume (c.c.)	Rate (mm^3/cm^2-min.)	Potential (Volts)	Temp °C (Avg.)	Pressure Corrected
5	1.53	1.53	153	- .964	24.0	701.7
10	3.82	2.29	229	- .974		mm Hg
15	6.53	2.71	271	- .978		
20	9.34	2.82	281	- .983		
25	12.56	3.22	322	- .989		
30	15.96	3.40	340	- .991		
35	19.52	3.56	356	- .992		
40	23.25	3.73	373	- .993		
45	26.82	3.57	357	- .995		
50	30.47	3.65	365	- .995		
55	34.29	3.82	382	- .997		
60	38.02	3.73	373	- .997		
65	41.67	3.65	365	- .997		
70	45.32	3.65	365	- .997		
75	48.97	3.65	365	- .997		
80	52.79	3.82	382	- .998		
85	56.69	3.90	390	- .998		
90	60.60	3.91	391	- .999		
95	64.67	4.07	407	- .999		
100	68.57	3.90	390	- 1.00		
105	72.82	4.25	425	- 1.00		
110	76.89	4.07	407	- 1.00		
115	80.71	3.82	382	- 1.00		

Average maximum rate of dissolution: 378.61 mm^3/cm^2-min.

Dissolution rate:	153	229	271	281	322	340	357
Avg. corresponding: potential, H_2 scale	-.683	-.693	-.697	-.702	-.708	-.710	-.713

	365	373	382	390	407	425
continued :	-.715	-.714	-.717	-.7185	-.7185	-.719

Table XLV

Potential measurement and rate of dissolution of Ti in 2N H_2SO_4 plus 2N NH_4F

Run No. 1

Time (Min.)	Volume H_2 (c.c.)	Volume (c.c.)	Rate (mm^3/cm^2-min.)	Potential (Volts)	Temp °C (Avg.)	Pressure Corrected
5	3.39	3.39	399	-.988	24.6	702.75
10	7.04	3.65	365	-1.00		mm Hg
15	10.86	3.82	382	-1.008		
20	14.76	3.90	390	-1.01		
25	18.83	4.07	407	-1.014		
30	22.99	4.16	416	-1.016		
35	27.31	4.32	432	-1.02		
40	31.72	4.41	441	-1.025		
45	35.88	4.16	416	-1.028		
50	40.29	4.41	441	-1.030		
55	44.70	4.41	441	-1.030		
60	49.20	4.50	450	-1.034		
65	53.60	4.40	440	-1.038		
70	58.10	4.50	450	-1.039		
75	62.77	4.67	467	-1.039		
80	67.35	4.58	458	-1.042		
85	72.01	4.66	466	-1.044		
90	76.76	4.75	475	-1.045		
95	81.68	4.92	492	-1.046		

Average maximum rate of dissolution: 429.89 mm^3/cm^2-min.

Dissolution rate:	339	365	382	390	407	416	432
Avg. corresponding potential, H_2 scale:	-.707	-.719	-.727	-.729	-.733	-.740	-.739

	441	450	458	466	475	492
continued:	-.750	-.756	-.761	-.761	-.764	-.765

Table XLVI

Potential measurement and rate of dissolution of Ti in 2N H_2SO_4 plus 2N NH_4F

Run No. 2

Time (Min.)	Volume H_2 (c.c.)	Volume (c.c.)	Rate (mm^3/cm^2-min.)	Potential (Volts)	Temp °C (Avg.)	Pressure Corrected
5	3.1	3.1	310	-.974	23.2	710.08
10	6.54	3.44	344	-.988		mm Hg
15	10.76	4.22	422	-.999		
20	15.07	4.31	431	-1.007		
25	19.63	4.56	456	-1.013		
30	24.28	4.65	465	-1.019		
35	29.28	5.00	500	-1.025		
40	34.44	5.16	516	-1.029		
45	39.61	5.17	517	-1.032		
50	45.04	5.43	543	-1.036		
55	50.29	5.25	525	-1.040		
60	55.80	5.51	551	-1.046		
65	61.48	5.68	568	-1.050		
70	67.17	5.69	569	-1.0534		
75	72.93	5.76	576	-1.057		
80	78.70	5.77	577	-1.061		
85	84.65	5.95	595	-1.065		

Average maximum rate of dissolution: 520.73 mm^3/cm^2-min.

Average maximum rate of dissolution for both runs: 474.32 mm^3/cm^2-min.

Dissolution rate:	310	344	422	431	456	465	500
Avg. corresponding: potential, H_2 scale	-.693	-.707	-.718	-.726	-.732	-.738	-.744
	517	525	543	551	569	577	595
continued:	-.750	-.759	-.755	-.765	-.771	-.778	-.784

Table XLVII

Potential measurement and rate of dissolution of Ti in 2N H_2SO_4 and 4N NH_4F

Run No. 1

Time (Min.)	Volume H_2 (c.c.)	Volume (c.c.)	Rate (mm^3/cm^2-min.)	Potential (Volts)	Temp °C (Avg.)	Pressure Corrected
5	4.86	4.86	486	-1.117	29.1	704.3
10	10.55	5.69	569	-1.117		mm Hg
15	16.25	5.70	570	-1.122		
20	21.77	5.52	552	-1.127		
25	37.47	5.70	570	-1.130		
30	33.16	5.69	569	-1.135		
35	38.86	5.70	570	-1.138		
40	44.39	5.53	553	-1.140		
45	49.91	5.52	552	-1.141		
50	55.36	5.45	545	-1.143		
55	60.80	5.44	544	-1.146		
60	65.99	5.19	519	-1.148		
65	71.35	5.63	563	-1.150		
70	76.38	5.03	503	-1.152		
75	80.73	4.35	435	-1.154		

Average maximum rate of dissolution: 550.15 mm^3/cm^2-min.

Dissolution rate:	435	486	503	519	536	545
Avg. corresponding potential, H_2 scale:	-.875	-.838	-.873	-.869	-.871	-.866

	552	570
continued:	-.857	-.849

Table XLVIII

Potential measurement and rate of dissolution of Ti in 2N H_2SO_4 and 4N NH_4F

Run No. 2

Time (Min.)	Volume H_2 (c.c.)	Volume (c.c.)	Rate (mm^3/cm^2-min.)	Potential (Volts)	Temp °C (Avg.)	Pressure Corrected
5	4.13	4.13	413	-1.114	23.4	710.1
10	8.78	4.65	465	-1.118		mm Hg
15	14.11	5.33	533	-1.120		
20	19.96	5.85	585	-1.127		
25	25.81	5.85	585	-1.128		
30	31.58	5.77	577	-1.131		
35	37.52	5.94	594	-1.136		
40	43.11	5.59	559	-1.137		
45	48.88	5.77	577	-1.140		
50	54.73	5.85	585	-1.144		
55	60.58	5.85	585	-1.146		
60	66.26	5.68	568	-1.149		
65	71.59	5.33	533	-1.150		
70	76.07	4.48	448	-1.152		
75	80.11	4.04	404	-1.154		
80	83.04	2.93	293	-1.154		

Average maximum rate of dissolution: 571 mm^3/cm^2-min.

Average maximum rate of dissolution for both runs: 560.58 mm^3/cm^2-min.

Dissolution rate:	293	404	413	448	465	533
Avg. corresponding: potential, H_2 scale	-.873	-.873	-.833	-.871	-.837	-.854

	559	568	577	585	594
continued:	-.856	-.868	-.855	-.855	-.855

Table XLIX

Potential measurement and rate of dissolution of Ti in 0.5N HF

Time (Min.)	Volume H_2 (c.c.)	Volume (c.c.)	Rate (mm^3/cm^2-min.)	Potential (Volts)	Temp °C (Avg.)	Pressure Corrected
10	2.34	2.34	117.0	-1.063	27.35	699.5
20	4.43	2.09	104.5	-1.062		mm Hg
30	6.19	1.76	88.0	-1.062		
40	7.70	1.51	75.5	-1.062		
50	9.70	2.00	100.0	-1.062		
60	11.21	1.51	75.5	-1.062		
70	13.30	2.09	104.5	-1.061		
80	14.81	1.51	75.5	-1.061		
90	16.40	1.59	79.5	-1.061		
100	17.90	1.50	75.0	-1.061		
110	19.49	1.59	79.5	-1.061		
120	21.00	1.51	75.5	-1.061		
130	21.75	.75	37.5	-1.061		
140	23.42	1.67	83.5	-1.06		
150	25.26	1.84	92.0	-1.061		
160	26.77	1.51	75.5	-1.061		
170	28.11	1.34	67.0	-1.061		
180	29.53	1.42	71.0	-1.06		
190	31.12	1.59	79.5	-1.06		
200	32.79	1.67	83.5	-1.06		
210	34.13	1.34	67.0	-1.06		
220	36.14	2.01	100.5	-1.06		
230	37.14	1.00	50.0	-1.06		
240	38.65	1.51	75.5	-1.059		
250	40.82	2.17	108.5	-1.058		
260	43.00	2.18	109.0	-1.058		
270	45.51	2.51	125.5	-1.058		
280	47.60	2.09	104.5	-1.058		

Average maximum rate of dissolution: 85.00 mm^3/cm^2-min.

Dissolution rate:	37.5	50.0	67.0	71.0	75.5	79.5	83.5
Avg. corresponding potential, H_2 scale:	-.781	-.78	-.78	-.78	-.781	-.781	-.78

	88.0	92.0	100.25	104.5	109	117	125.5
continued:	-.782	-.781	-.781	-.78	-.778	-.783	-.778

Table L

Potential measurement and rate of dissolution of Ti in 2N HF

Time (Min.)	Volume H_2 (c.c.)	Volume (c.c.)	Rate (mm^3/cm^2-min.)	Potential (Volts)	Temp °C (Avg.)	Pressure Corrected
5	4.91	4.91	491	-1.064		
10	9.99	5.08	508	-1.064		
15	15.24	5.25	525	-1.063		
20	20.66	5.42	542	-1.062		
25	25.66	5.00	500	-1.06		
30	30.99	5.33	533	-1.06		
35	36.41	5.42	542	-1.06		
40	41.83	5.42	542	-1.059		
45	47.42	5.59	559	-1.06		
50	53.60	6.18	618	-1.061		
55	60.12	6.52	652	-1.061		
60	66.98	6.86	686	-1.061		
65	73.84	6.86	686	-1.061		
70	81.04	7.20	720	-1.061		

Average maximum rate of dissolution: 578.86 mm^3/cm^2-min.

Dissolution rate:	491	500	508	525	533	542
Avg. corresponding potential, H_2 scale:	-.784	-.780	-.784	-.783	-.780	-.780

	559	618	652	686	720
continued:	-.780	-.781	-.781	-.781	-.781

Table LI

Potential measurement and rate of dissolution of Ti in 3N HF

Time (Min.)	Volume H_2 (c.c.)	Volume (c.c.)	Rate (mm^3/cm^2-min.)	Potential (Volts)	Temp °C (Avg.)	Pressure Corrected
5	10.57	10.47	1057	-1.055	24.4	706.0
10	22.51	11.94	1194	-1.057		mm Hg
15	34.79	12.28	1228	-1.058		
20	47.41	12.62	1262	-1.058		
25	60.03	12.62	1262	-1.058		
30	72.99	12.96	1296	-1.059		
35	85.57	12.58	1258	-1.059		

Average maximum rate of dissolution: 1250 mm^3/cm^2-min.

Dissolution rate:	1057	1194	1228	1258	1262	1296
Avg. corresponding potential, H_2 scale:	-.774	-.776	-.777	-.778	-.777	-.778

(v) Conclusions:

The obvious correlation between the rate of dissolution and potential of the Ti electrode in 2N H_2SO_4 with NH_4F added, was that as the strength of the HF concentration formed from NH_4F additions increased, and consequently the rate of dissolution, the potential decreased and became less noble. This seemed to indicate that a higher rate of dissolution was associated with a more negative potential. However, with HF alone, the rate of dissolution increased with increasing strength of acid, but the potential remained practically unchanged for all acid concentrations. These results for a titanium electrode in HF are practically identical to those obtained by Straumanis and Chen [2],

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2) Straumanis, M. E., and Chen, P. C., op. cit. 238

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being in the neighborhood of -0.780 volts, corrected to the hydrogen scale at 25° C. An earlier paper by Botts [9] and his associates

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9) Botts, E. D., and Krauskoff, F. C., Some Electrochemical Studies of Titanium, Journal of Physical Chemistry, 31^2, 1404-19, (1927)

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pointed out that they found the titanium electrode does not act as hydrogen electrode, and a little HF added to a solution strongly acid with H_2SO_4 would increase the electrode potential enormously. They also mentioned from their potential measurements that titanium in the ordinary cell was less noble than hydrogen.

These facts appear to correlate in that a rate of dissolution which follows a straight line function, such as does Ti in HF, has no appreciable change in potential. While those which follow a somewhat more curved line, such as with varying additions of NH_4F in H_2SO_4, the potential becomes less noble as the rate of dissolution increases. A comparison of the rates of dissolution is shown in Figure 4.

Still greater amounts of NH_4F than 4N NH_4F gave erratic results as to plotting them on a curve, but did show that the potential continued to become less noble, although some type of passivation apparently took place and greatly reduced the rate of dissolution of the titanium.

PART II

SECTION G

Potential Measurements and Dissolution Rates of Titanium on Adding Large Amounts of Ammonium Fluoride to Various Acids.

(i) Method, Apparatus, and Procedure:

The equipment used for this series of investigations was similar to that used in the previous section. The connections to the potentiometer were also similar.

Several preliminary tests were made first in a beaker open to the air. An unmeasured amount of 2N H_2SO_4 was placed in the beaker and additions of NH_4F made. After each NH_4F addition the mixture was stirred until the NH_4F was all in solution, then a potential reading for the Ti electrode was taken. No attempt was made to measure the amount of NH_4F added. Additions of NH_4F were made, and potential readings taken until the lowest potential reading that could be obtained was reached. The readings were continued until a constant potential reading was arrived at, which did not vary appreciable with further additions of NH_4F. The same test was run with 2N HF in place of 2N H_2SO_4.

Quantitative tests were made next in the closed flask in a nitrogen atmosphere in exactly the same manner as previously described in SECTION E, with the rates of dissolution and potential measurements of the titanium electrode being recorded at definite intervals. Thirty

grams of NH_4F was dissolved in sufficient acid to give a total volume of solution sufficient to cover the titanium electrode and immerse the stirring paddle. In the flask used, this was 140 ml. of 1N H_2SO_4 and 136.5 ml. of 1N HF. The thirty grams of NH_4F dissolved in the acids brought the total volume of solution to about 160 c.c., and this total volume was measured after each run so that an approximation could be made of the NH_4F resulting from the NH_4F added. Thirty grams of NH_4F in the acid mixture was considered a sufficient quantity to obtain the maximum negative potential reading of the titanium electrode.

It was noticed after the run was completed that the titanium electrode was still bright and shiny when taken from the flask, but as soon as the acid film was washed off the surface it immediately oxidized in the air to a metallic blue colour. To learn something of this phenomenon, the electrode was at once placed in a beaker in air, containing the same acid mixture as used in the flask in the nitrogen atmosphere, and potential readings were made until a constant potential was reached.

As a further step in trying to explain this phenomenon, a test was made using 165 c.c. of a mixture of 1N HF plus 30 grams of NH_4F, with compressed air being blown into the flask, after the potential readings had levelled off. This compressed air displaced the nitrogen atmosphere with one containing oxygen, to see if that would influence the titanium potential readings.

(ii) Calculations:

A sample calculation to determine the approximate concentration of NH_4F

Total volume of solution in flask	158 c.c.
Molecular weight of NH_4F	37
Amount of NH_4F added	30 grams in 158 c.c.
Approximate N HF of the solution from the NH_4F added	$\frac{30}{37} \times \frac{1000}{158} = 5.126N\ NH_4F$

(iii) Results:

The preliminary tests made in air by adding NH_4F in quantity to 2N H_2SO_4 and 2N HF agave a maximum negative potential reading approximately the same for both acids; the results are tabulated in Tables LII and LIII. In Figure 10 the potential in volts according to the H_2 scale is plotted against the increasing amounts of NH_4F added. The chief difference between the two tests was that, while in both cases the titanium electrode became dark and passive when the maximum negative potential was reached and the potential rose very rapidly from that point, in the case of the 2N HF plus NH_4F the potential rose only to -0.778 volts, which is roughly the potential of the titanium electrode in pure HF. The potential then remained constant at that value. However, with the 2N H_2SO_4 plus NH_4F the potential rose rapidly to a minimum negative potential of -0.671 volts, then on the addition of more NH_4F slowly dropped again and became constant at a potential of -0.782 volts, almost that of a titanium electrode in pure HF.

In all cases the hydrogen evolution was strong until the maximum negative potential was reached, whereupon the bright titanium electrode became quite dark and lustreless, and the H_2 evolution very nearly stopped altogether. On the addition of more NH_4F the evolution began again at a very slow rate, but never did approach its initial

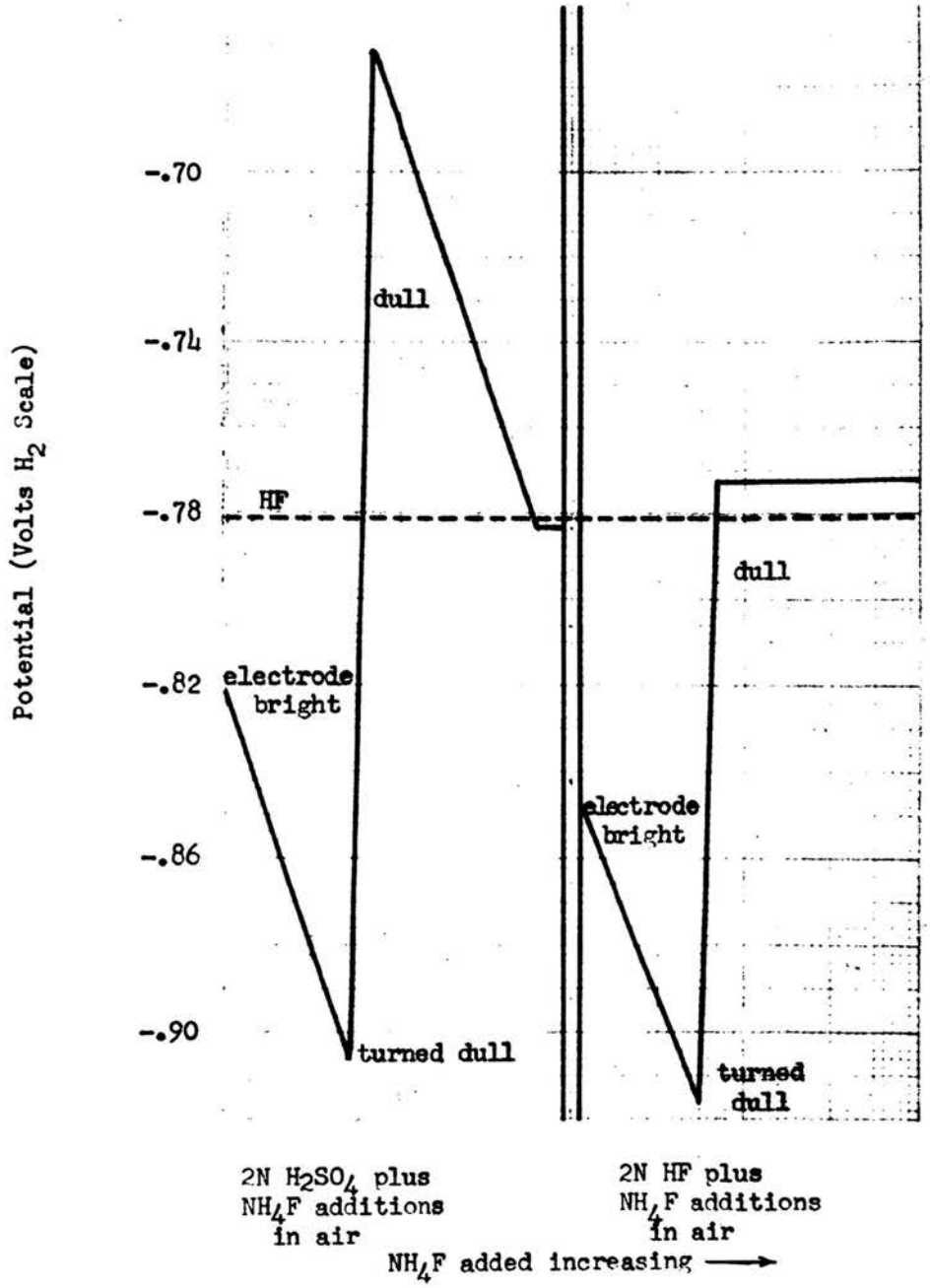


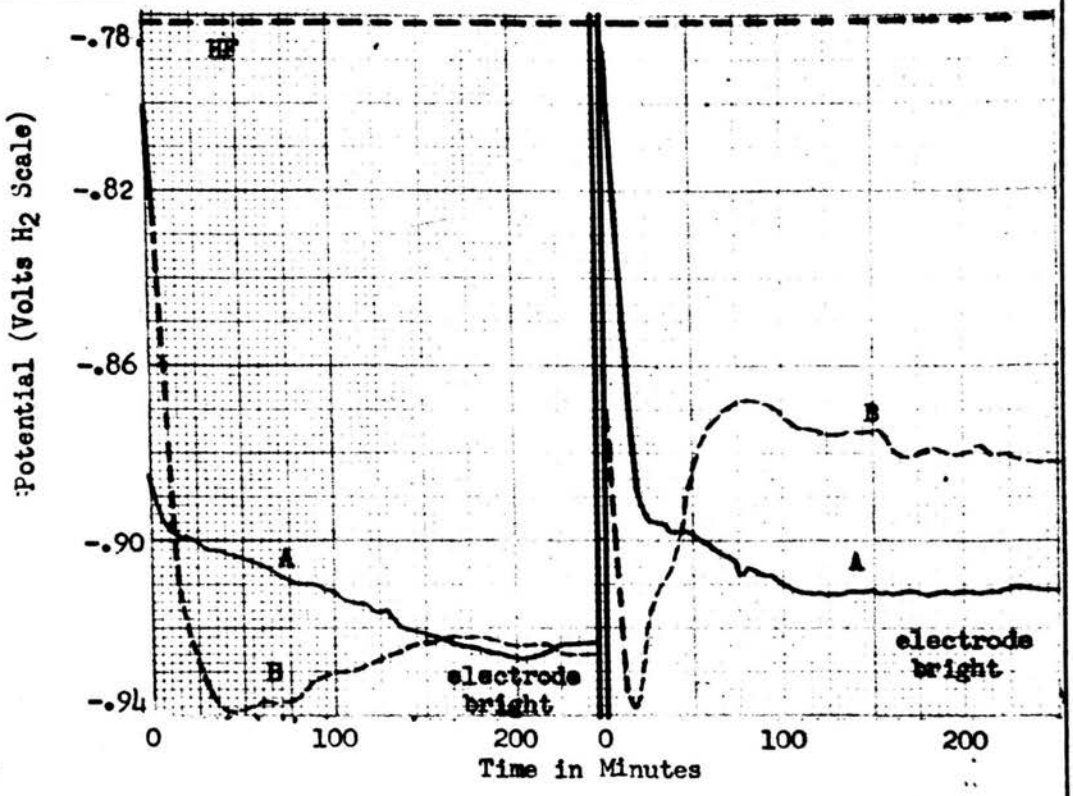
Figure 10

Potential measurements of a Ti electrode in acid electrolytes with increasing amounts of NH_4F added.

velocity. Also the colour of the solution, which was clear to begin with, gradually changed to a progressively darker yellowish-green as NH_4F was added, until the maximum negative potential was reached. Then the solution cleared, became colourless once again, and remained so for the rest of the test.

The results of the quantitative tests are given in Tables LIV to LVII, and Figure 11. The results with both 2N H_2SO_4 and 1 N HF are fairly much alike. The potentials dropping rapidly with time to a maximum negative potential value, then increasing slightly and remaining constant. Or else, the potentials dropped somewhat more slowly to a maximum negative value, slightly lower than in the first case, and remained fairly constant there with time.

On taking the still shiny surfaced titanium electrode out of the nitrogen atmosphere and putting it in a beaker in air containing the same acid mixture as used in the nitrogen atmosphere, after first washing the electrode with distilled water to clean off the acid film and permit the titanium surface to oxidize, the same general trend followed with both acid mixtures, as shown in Tables LVIII to LIX and Figure 12. The potential dropped swiftly to a maximum negative value, the electrode became dark and passive with the hydrogen evolution slowing drastically, then the potential rose instantly to a minimum negative value, dropped more slowly to a maximum negative value approximately the same as at the first, and remained constant there. When the drop from the minimum negative value began, the H_2 evolution increased slightly, and remained at a steady, very slow rate. The acid



1N HF plus 30 grams NH_4F, in N_2 atmosphere

2N H_2SO_4 plus 30 grams NH_4F, in N_2 atmosphere

Figure 11

Potential measurements of a Ti electrode in HF and H_2SO_4 plus 30 grams of NH_4F, in a nitrogen atmosphere.

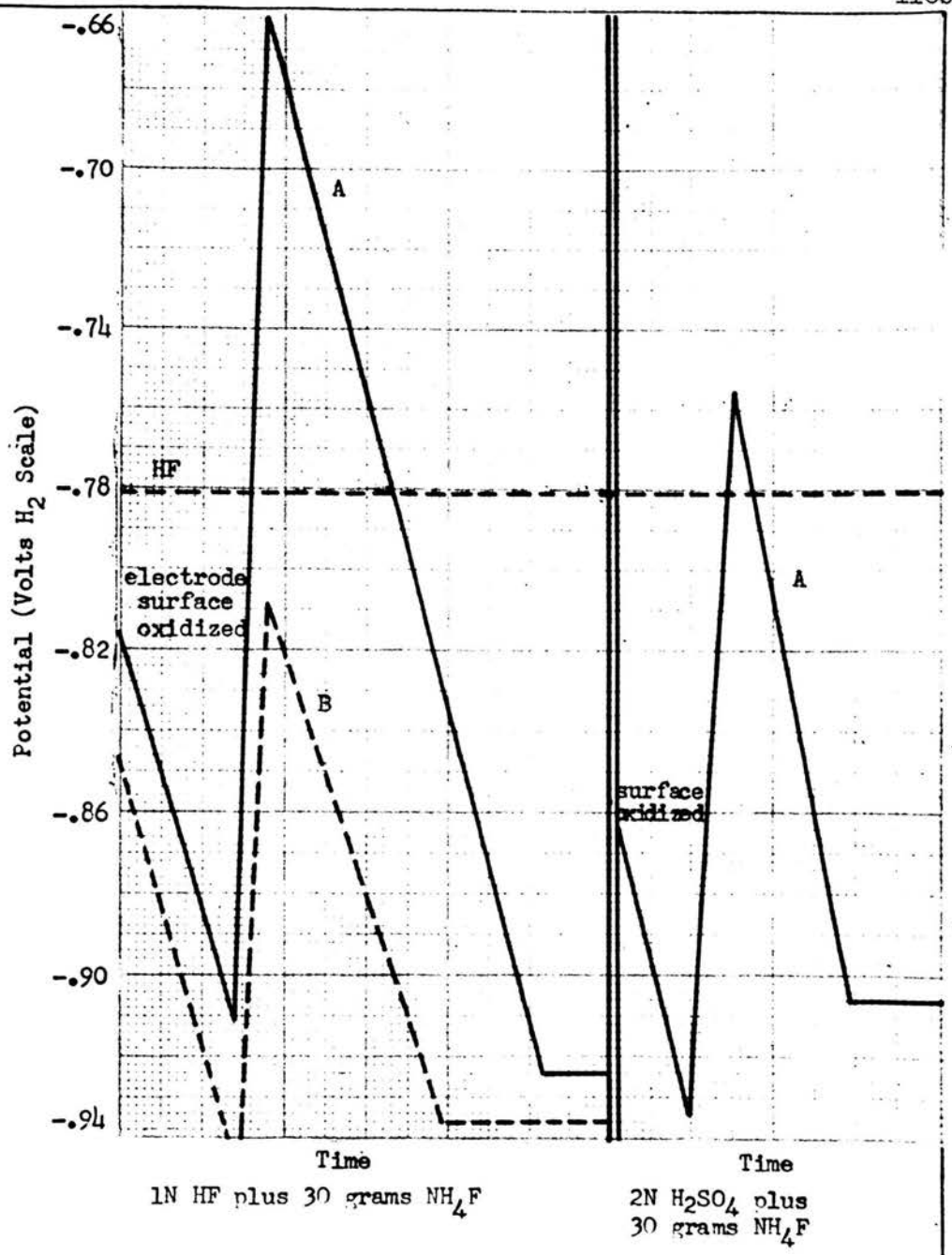


Figure 12

Potential measurements of a Ti electrode with oxidized surface in HF and H_2SO_4 plus 30 grams of NH_4F, in air.

solution also again changed from a greenish-yellow colour to colourless at the maximum negative potential, and remained colourless.

The results obtained on first using a nitrogen atmosphere, then when the potential readings had levelled off to a fairly constant value sending a stream of compressed air into the flask to change the atmosphere from nitrogen to oxygen, are shown in Table LX, and Figure 13. No appreciable change could be seen in the potential readings on changing the atmosphere in the flask from nitrogen to oxygen, though the titanium surface was dull and oxidized when taken from the acid mixture.

Table LII

Potential measurements of Ti electrode in 2N H_2SO_4 with increasing additions of NH_4F

NH_4F increasing	Run No. 1 Potential H_2 Scale		Run No. 2 Potential H_2 Scale		Run No. 3 Potential H_2 Scale	
	-.689		-.595		-.579	
	-.731		-.639		-.623	
	-.771		-.666		-.625	
	-.807		-.724		-.659	
	-.845		-.741		-.685	
	-.864		-.793		-.709	
	-.880		-.805		-.745	
	-.896		-.841		-.791	
	-.908		-.858		-.843	
	-.909	*Max.	-.885		-.875	
	-.685	Passive	-.902		-.899	
	-.709		-.905	*Max.	-.917	*Max.
	-.729		-.679	Passive	-.649	Passive
	-.755		-.707		-.677	
	-.762		-.715		-.707	
	-.773		-.735		-.731	
	-.781		-.750		-.755	
	-.787		-.764		-.759	
	-.795		-.775		-.759	constant
	-.796		-.778		-.755	
	-.799		-.779			
	-.805		-.778	constant		
	-.809		-.778			
	-.807					
	-.809	constant				

Average maximum negative potential: -0.910 Volts
Average passive negative potential: -0.671 Volts
Average constant negative potential: -0.782 Volts

Table LIII

Potential measurements of Ti electrode in 2N HF with increasing additions of NH_4F

Run No. 1

NH_4F increasing	Potential H_2 scale	
	-.774	
	-.766	
	-.835	
	-.863	
	-.886	
	-.915	*Max.
	-.909	Passive
	-.778	
	-.778	
	-.769	
	-.768	
	-.779	
	-.764	constant
	-.759	
	-.773	

Maximum negative potential : -0.915 Volts
Passive negative potential : -0.778 Volts
Constant negative potential: -0.771 Volts

Table LIV

Potential measurements and rate of dissolution of Ti electrode in 2N H_2SO_4 plus 30 grams NH_4F

Run No. 1

Time (Min.)	Volume H_2 (c.c.)	Volume (c.c.)	Rate (mm^3/cm^2-min.)	Potential H_2 scale	Temp ^oC (Avg.)	Barometer Corrected
5	.84	.84	84	-.814	27.0	702.25
"	1.51	.67	67	-.862		mm Hg
"	1.85	.34	34	-.878		
	2.19	.34	34	-.892	140 ml. 2N H_2SO_4	
	2.69	.50	50	-.896	+30 gms. NH_4F	
	3.19	.50	50	-.896	5.77 N with	
	3.57	.38	38	-.898	respect to NH_4F	
	3.91	.34	34	-.898		
	4.37	.46	46	-.899		
	4.71	.34	34	-.899		
	4.96	.25	25	-.900		
	5.42	.46	46	-.902		
	5.80	.38	38	-.903		
	6.10	.30	30	-.903		
	6.39	.29	29	-.907		
	6.68	.29	29	-.905		
	7.15	.47	47	-.907		
	7.48	.33	33	-.908		
	7.73	.25	25	-.908		
	8.07	.34	34	-.908		
	8.41	.34	34	-.911		
	8.74	.33	33	-.911		
	9.08	.34	34	-.911		
	9.33	.25	25	-.911		
	9.58	.25	25	-.911		
	9.84	.26	26	-.911		
	10.26	.42	42	-.911		
	10.51	.25	25	-.911		
	10.76	.25	25	-.911		
	11.01	.25	25	-.912		
	11.27	.26	26	-.911		
	11.52	.25	25	-.912		
	11.77	.25	25	-.911		
	12.11	.33	33	-.911		
	12.44	.33	33	-.911		
	12.70	.26	26	-.912		

Table LIV Continued

12.95	.25	25	-.912
13.12	.17	17	-.911
13.54	.42	42	-.912
13.79	.25	25	-.911
13.96	.17	17	-.911
14.12	.16	16	-.911
14.29	.17	17	-.911
14.46	.17	17	-.910
14.71	.25	25	-.910
14.97	.26	26	-.910
15.13	.16	16	-.910
15.30	.17	17	-.910
15.47	.17	17	-.910
15.64	.17	17	-.910
15.81	.17	17	-.911

Maximum negative potential: -0.912 volts
Average maximum rate of dissolution: 35.14 mm^3/cm^2-min.

Rate of dissolution:	7	25	29	34	38	42	46	50
Corresponding potential:	-.910	-.910	-.905	-.906	-.900	-.911	-.902	-.897

Table LV

Potential measurements and rate of dissolution of Ti electrode in 2N H_2SO_4 plus 30 grams NH_4F

Run No. 2

Time (Min.)	Volume H_2 (c.c.)	Volume (c.c.)	Rate (mm^3/cm^2-min.)	Potential H_2 scale	Temp °C (Avg.)	Barometer Corrected
5	.34	.34	34	-.914	25.0	705.66
"	.51	.17	17	-.912		mm Hg
"	.68	.17	17	-.907		
	.85	.17	17	-.900	165 c.c. of mixture	
	1.02	.17	17	-.888	2N H_2SO_4 + 30g NH_4F	
	1.02	0	0	-.880	4.91N with respect	
	1.19	.17	17	-.875	to NH_4F	
	1.19	0	0	-.872		
	1.36	.17	17	-.870		
	1.45	.08	8	-.868		
	1.53	.09	9	-.868		
	1.62	.09	9	-.868		
	1.62	0	0	-.868		
	1.70	.08	8	-.869		
	1.70	0	0	-.870		
	1.79	.09	9	-.871		
	1.87	.08	8	-.873		
	1.87	0	0	-.874		
	1.93	.06	6	-.874		
	1.99	.06	6	-.874		
	2.05	.06	6	-.875		
	2.12	.07	7	-.875		
	2.19	.07	7	-.875		
	2.25	.06	6	-.875		
	2.38	.13	13	-.875		
	2.47	.09	9	-.874		
	2.55	.08	8	-.876		
	2.64	.09	9	-.878		
	2.76	.12	12	-.880		
	2.89	.13	13	-.880		
	2.98	.09	9	-.878		
	3.23	.25	25	-.878		
	3.32	.09	9	-.878		
	3.40	.08	8	-.880		
	3.57	.17	17	-.880		
	3.74	.17	17	-.880		

Table LV Continued

3.91	.17	17	-.878
4.00	.09	9	-.878
4.17	.17	17	-.880
4.29	.12	12	-.880
4.42	.13	13	-.880
4.59	.17	17	-.881
4.76	.17	17	-.881
4.93	.17	17	-.881
5.10	.17	17	-.882
5.27	.17	17	-.883
5.44	.17	17	-.882
5.70	.26	26	-.883
5.87	.17	17	-.883
6.04	.17	17	-.883
6.20	.16	16	-.883
6.38	.18	18	-.883
6.63	.25	25	-.883
6.80	.17	17	-.891
6.97	.17	17	-.889
7.14	.17	17	-.888
7.31	.17	17	-.886
7.48	.17	17	-.886
7.65	.17	17	-.885
7.91	.26	26	-.885

Maximum negative potential: -0.914 volts
Average maximum rate of dissolution: 20.53 mm^3/cm^2-min.

Rate of dissolution:	6	9	13	17	26
Corresponding potential:	-.875	-.874	-.879	-.885	-.881

Table LVI

Potential measurements and rate of dissolution of Ti electrode in 1N HF plus 30 grams NH_4F

Run No. 1

Time (Min.)	Volume H_2 (c.c.)	Volume (c.c.)	Rate (mm^3/cm^2-min.)	Potential H_2 scale	Temp °C (Avg.)	Barometer Corrected
1½	.845	0	0	-.890	27.0	705.33
"	.845	0	0	-.897		mm Hg
"	.929	.08	26.7	-.899		
	.929	0	0	-.900	136.5 c.c. 1N HF	
	1.013	.08	26.7	-.900	+30 gms. N H_4F	
	1.098	.08	26.7	-.902	5.92 N	
	1.182	.08	26.7	-.903	with respect to NH_4F	
	1.267	.08	26.7	-.903		
	1.351	.08	26.7	-.9035		
	1.346	.08	26.7	-.904		
	1.52	.08	26.7	-.904		
	1.52	0	0	-.906		
	1.605	.08	26.7	-.907		
	1.689	.08	26.7	-.908		
	1.731	.04	13.3	-.909		
	1.731	0	0	-.909		
	1.858	.13	43.3	-.910		
	1.90	.04	13.3	-.910		
	2.027	.13	43.3	-.911		
	2.027	0	0	-.911		
	2.111	.08	26.7	-.913		
	2.196	.08	26.7	-.914		
	2.280	.08	26.7	-.914		
	2.365	.08	26.7	-.914		
	2.534	.17	56.7	-.917		
5	2.703	.17	17	-.915		
"	2.872	.17	17	-.917		
"	3.083	.21	21	-.921		
	3.294	.21	21	-.921		
	3.547	.25	25	-.921		
	3.801	.25	25	-.922		
	4.012	.21	21	-.923		
	4.223	.21	21	-.923		
	4.392	.17	17	-.924		
	4.645	.25	25	-.924		
	4.856	.21	21	-.926		

Table LVI Continued

5.025	.17	17	-.926
5.236	.21	21	-.926
5.405	.17	17	-.927
5.574	.17	17	-.927
5.573	.17	17	-.927
5.912	.17	17	-.927
6.081	.17	17	-.927
6.250	.17	17	-.925
6.419	.17	17	-.925
6.588	.17	17	-.924
6.757	.17	17	-.924
6.925	.17	17	-.924
7.094	.17	17	-.923
7.263	.17	17	-.922
7.432	.17	17	-.922
7.601	.17	17	-.922
7.77	.17	17	-.922
7.94	.17	17	-.922

Maximum negative potential: -0.927 volts
Average maximum rate of dissolution: 24.0 mm^3/cm^2-min.

Rate of dissolution:	17	21	25
Corresponding potential:	-.923	-.923	-.922

Table LVII

Potential measurements and rate of dissolution of Ti electrode in 1N HF plus 30 grams NH_4F

Run No. 2

Time (Min.)	Volume H_2 (c.c.)	Volume (c.c.)	Rate (mm^3/cm^2-min.)	Potential H_2 scale	Temp °C (Avg.)	Pressure Corrected
5	.34	.34	34	-.804	26.5	703.65
"	.51	.17	17	-.888		mm Hg
"	.84	.33	33	-.910		
	1.01	.17	17	-.920	165 c.c. mixture of	
	1.27	.26	26	-.927	1N HF + 30 grams NH_4F	
	1.53	.25	25	-.934	4.91 N with respect	
	1.86	.34	34	-.937	to NH_4F	
	2.07	.21	21	-.939		
	2.24	.17	17	-.939		
	2.53	.29	29	-.939		
	2.87	.34	34	-.938		
	3.08	.21	21	-.937		
	3.32	.24	24	-.937		
	3.56	.24	24	-.937		
	3.81	.25	25	-.937		
	4.05	.24	24	-.937		
	4.22	.17	17	-.933		
	4.39	.17	17	-.932		
	4.56	.17	17	-.931		
	4.73	.17	17	-.930		
	4.94	.21	21	-.930		
	5.10	.17	17	-.929		
	5.27	.17	17	-.929		
	5.44	.17	17	-.928		
	5.74	.30	30	-.928		
	5.91	.17	17	-.927		
	6.03	.13	13	-.926		
	6.16	.13	13	-.925		
	6.33	.17	17	-.924		
	6.50	.17	17	-.923		
	6.67	.17	17	-.923		
	6.83	.17	17	-.923		
	7.09	.25	25	-.923		
	7.34	.25	25	-.922		
	7.51	.17	17	-.922		
	7.68	.17	17	-.922		

Table LVII Continued

7.85	.17	17	-.922
8.02	.17	17	-.922
8.14	.13	13	-.923
8.27	.13	13	-.924
8.44	.17	17	-.924
8.61	.17	17	-.924
8.94	.33	33	-.924
9.11	.17	17	-.924
9.28	.17	17	-.925
9.45	.17	17	-.925
9.62	.17	17	-.926
9.79	.17	17	-.926
9.96	.17	17	-.926
10.13	.17	17	-.926

Maximum negative potential: -.939 volts
Average maximum rate of dissolution: 24.14 mm^3/cm^2-min.

Rate of dissolution:	8	13	17	21	24	30	34
Corresponding potential:	-.926	-.924	-.925	-.935	-.934	-.933	-.933

Table LVIII

Potential measurements of Ti electrode in air in 2N H_2SO_4 plus 30 grams of NH_4F

Run No. 1		Run No. 2	
Potential H_2 scale	Remarks	Potential H_2 scale	Remarks
-.934 *	max. neg. pot.	-.900	good H_2 evolution
-.922		-.902 *	max. neg. pot.
-.756	ti passive	-.880	ti passive
-.760	H_2 evolution	-.876	H_2 evolution
-.806	slow	-.868	slow
-.840		-.882	
-.866		-.900	
-.888		-.900	
-.894		-.900	
-.896		-.905	
-.897		-.905	
-.899		-.905	
-.901		-.888	
-.901		-.888	
-.901		-.885	
-.903		-.883	
-.904		-.882	
-.906		-.882	
-.906		-.882	
-.906		-.882	

Table LIX

Potential measurements of Ti electrode in air in 1N HF plus 30 grams of NH_4F

Run No. 1		Run No. 2	
Potential H_2 scale	Remarks	Potential H_2 scale	Remarks
-.780	good H_2 solution	-.940	
-.910 *	max. neg. pot.	-.942 *	good H_2 evolution
-.660	ti passive	-.808	max. neg. pot.
-.883	very slight	-.853	ti passive
-.893	H_2 evolution	-.888	very slight
-.901	"	-.898	H_2 evolution
-.904	"	-.908	
-.908		-.914	
-.913		-.914	
-.917		-.914	
-.919		-.919	
-.921		-.923	
-.922		-.926	
-.922		-.930	
-.922		-.930	
-.922		-.932	
		-.933	
		-.933	
		-.933	

Table LX

Potential measurements and rate of dissolution of Ti electrode in 1N HF plus 30 grams NH_4F N_2 atmosphere, then O_2 atmosphere.

Time (Min.)	Volume H_2 (c.c.)	Volume (c.c.)	Rate (mm^3/cm^2-min.)	Potential H_2 scale	Temp °C (Avg.)	Barometer Corrected
seconds				-.954		
"				-.780		
"				-.786		
"				-.858		
5	.25	.25	25	-.904	28.0	702.61
"	.59	.34	34	-.919		mm Hg
"	.92	.33	33	-.933		
	1.34	.42	42	-.938	165 c.c. mixture	
	1.68	.34	34	-.943	of 1N HF +	
	2.01	.33	33	-.942	30 grams NH_4F	
	2.43	.42	42	-.943	4.91 with	
	2.77	.34	34	-.942	respect to NH_4F	
	3.10	.33	33	-.940		
	3.44	.34	34	-.939		
	3.86	.42	42	-.938		
	4.11	.25	25	-.936		
	4.28	.17	17	-.934	N_2 atmosphere	
	4.69	.41	41	-.932		
	4.95	.26	26	-.930		
	5.21	.26	26	-.928		
	5.47	.26	26	-.926		
	5.73	.26	26	-.924		
	5.99	.26	26	-.922		
	6.25	.26	26	-.920		
	6.51	.26	26	-.918		
	6.77	.26	26	-.918		
	7.04	.27	27	-.914		
	7.38	.34	34	-.918		
	7.54	.16	16	-.910		
	7.80	.25	25	-.908		
	8.05	.25	25	-.906		
	8.30	.25	25	-.903		
	8.55	.25	25	-.903		

Table LX Continued

8.72	.17	17	-.902
8.89	.17	17	-.902
9.06	.17	17	-.903
9.22	.16	16	-.906
9.47	.25	25	-.908
9.60	.13	13	-.911
9.81	.21	21	-.913
10.06	.25	25	-.913
10.31	.25	25	-.917
10.56	.26	26	-.919
10.82	.25	25	-.919
11.07	.25	25	-.920
11.40	.33	33	-.921
11.57	.17	17	-.921
11.91	.34	34	-.921
12.16	.25	25	-.921
12.41	.25	25	-.921

-.922	O_2 atmosphere,
-.920	stream of compressed
-.920	air bubbled into
-.920	acid mixture.
-.920	
-.920	
-.921	
-.921	
-.921	

-.921	O_2 atmosphere
-.921	acid in flask left
-.921	open to air.
-.921	
-.921	
-.921	

Maximum negative potential: -.943 volts.
Average maximum rate of dissolution: 32.56 mm^3/cm^2-min.

Rate of dissolution:	13	17	21	25	34	42
Corresponding potential:	-.911	-.911	-.913	-.917	-.932	-.938

(iv) Conclusions:

In every case, when the investigation was made in air, after a certain quantity of NH_4F was added to the acid being used, whether H_2SO_4 or HF, the titanium electrode turned dark and became passive, with the rate of evolution of hydrogen falling off nearly to a complete halt, and with a corresponding rise (Figure 10) in the negative potential reading. It can be seen from the sudden colour change of the titanium electrode from a shiny surface to a dark surface that some sort of surface film formed on the titanium. Also in every case in air, the acid mixture first turned a greenish-yellow colour until the maximum negative potential was reached, which would indicate some $Ti F_3$ complex was present. Then after this maximum potential was reached, and while the potential rose to a minimum negative potential and dropped again to a constant potential reading, the solution cleared and became colourless, which would seem to indicate that some $Ti F_4$ complex was present. The gradual climb of the potential measurements from a minimum negative value, accompanied with a slow evolution of hydrogen shows that the surface film formed is not too long enduring. Apparently too, the acid solution must be exposed to air and oxidized to form this complex surface film, for when tests were run in a nitrogen atmosphere (Figure 13) no such phenomenon was observed, and the potential dropped to a maximum negative potential and stayed fairly constant there. However, the electrodes when removed from the flask after these runs in a nitrogen atmosphere were still bright and shiny,

displaying no discolouring surface film. Immediately on washing with water though, the fresh titanium surface oxidized in the air, and a series of potential measurements made at once on this oxidized surface in a beaker exposed to the air, gave a very similar set of graphs to that obtained when the potential measurements were made on increasing the quantity of NH_4F added to an acid solution in air. The greatest exception between the two sets of graphs (Figure 12), was that the oxidized titanium surface finally settled at a more anodic constant negative potential.

It may have been that the acid mixture used in the test with first a nitrogen atmosphere, then an oxygen atmosphere, was sufficiently oxidized ($Ti^{3+} \rightarrow Ti^{4+}$) that no appreciable difference was noticed in potential readings after the atmosphere was changed to oxygen. However, in this case, as in the tests run in air, the titanium surface was dark and oxidized when examined after the run was completed. This may have been caused by different oxidation and hydrolysis products forming on the surface of the Ti, due to the diffusion of oxygen to the surface of the metal.

PART II

SECTION H

Potential Measurements of an Anodically Polarized Titanium Electrode in Hydrofluoric Acid Plus Ammonium Fluoride.

It was of interest to determine why the passivation of Ti, described in the previous chapter, occured. There are three possible explanations:

(1) Changes in the surface of the Ti during dissolution cause potential changes and lead to a decrease in rate of dissolution.

(2) The resistance of the acid mixture is increased by the additions of NH_4F.

(3) There is an increase in the overvoltage of the local cathodes in the Ti, because of some influence from the NH_4F added.

All three of these possibilities can be considered by using a model element, Ti-HF-Pt, short-circuited through a milliammeter and variable resistance.

The changes of the potential of Ti versus current density are described in this chapter.

(i) Method and Apparatus:

The apparatus and electrical connections for this investigation, as shown in Figure 14, consisted of a titanium electrode, a platinized

platinum electrode, the same agar 1N KCl bridge, calomel half cell and recording potentiometer as used before, a variable resistance box, and a D. C. Weston type milliammeter (Model 1, No. 59194). Two kind of titanium electrodes were used, one being Remington Arms Ti 2 cm. square and the other Battelle Memorial Institute titanium 1/2 cm. square. Both electrodes were ground to exact size and mounted in bakelite, as previously described, so that their surfaces exposed were exactly 2 square cm., and 1/2 square cm., respectively. A platinum electrode with a 2 square cm. surface exposed was made in the same way, and platinized according to the method recommended by Findlay 10).

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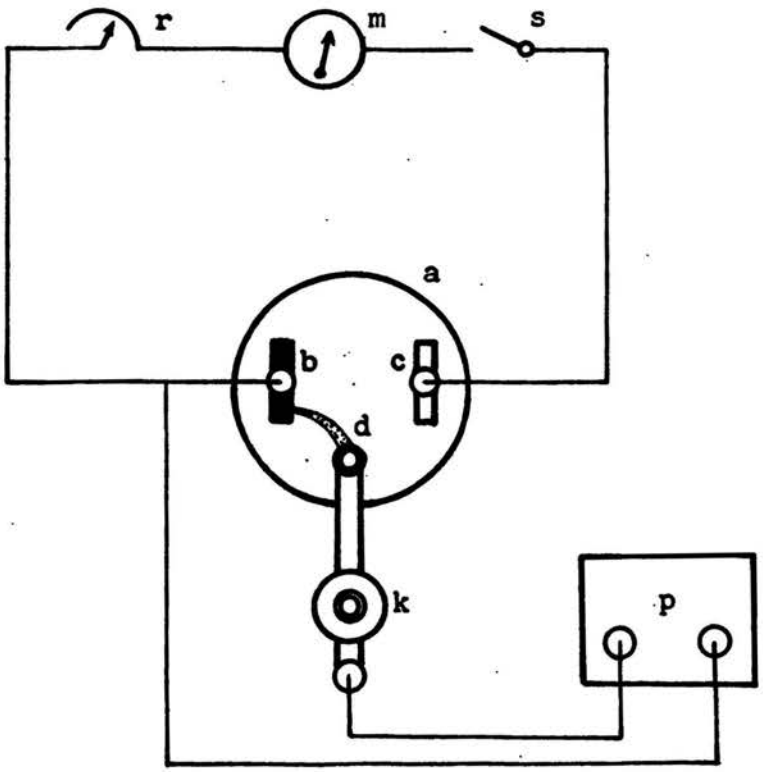
10) Findlay, A., Practical Physical Chemistry, Longmans, Green and Co., London, p. 162, (1941)

(ii) Procedure:

The tests were conducted in a beaker open to the air, and the Remington Arms titanium electrode was used first. After the apparatus was connected as in Figure 14, a sufficient volume of exactly 1N HF in which 30 grams of NH_4F had been dissolved was added to the beaker to entirely cover the two electrodes. The distance between the platinized platinum and titanium electrodes was 15 mm. The switch was left open, removing the platinized platinum and milliammeter from the circuit, and the potential of the titanium electrode alone measured until the potential had passed its maximum and minimum negative values and settled at a constant reading. The switch was closed, bringing



a - beaker
b - Ti electrode
c - Pt electrode
d - capillary tube from calomel cell
k - calomel cell
p - potentiometer
r - variable resistance
m - milliammeter
s - switch

Figure 14

Apparatus for potential measurements of a polarized Ti electrode.

the platinized platinum and milliammeter into the circuit, and with the resistance box set at zero resistance several simultaneous readings were made of potential and current density. Then the switch was opened once again and only the potential of the titanium electrode was measured for a few more readings. This procedure was repeated in 2N HF plus 30 grams of NH_4F, and in 4N HF plus 30 grams of NH_4F.

The method of procedure in the 4N HF plus 30 grams of NH_4F was varied slightly in that after the current density reached a fairly constant value the resistance of the box was used to decrease the current density in increments, with potential measurements being made in each instance. Then as before, the switch was opened and potential readings were taken on the titanium electrode alone.

The procedure followed with the Battelle Institute titanium was the same as that used for the Remington Arms titanium electrode in 4N HF plus 30 grams of NH_4F, and the acids used were of the same strength, 1N HF plus 30 grams NH_4F, 2N HF plus 30 grams of NH_4F, and 4N HF plus 30 grams of NH_4F.

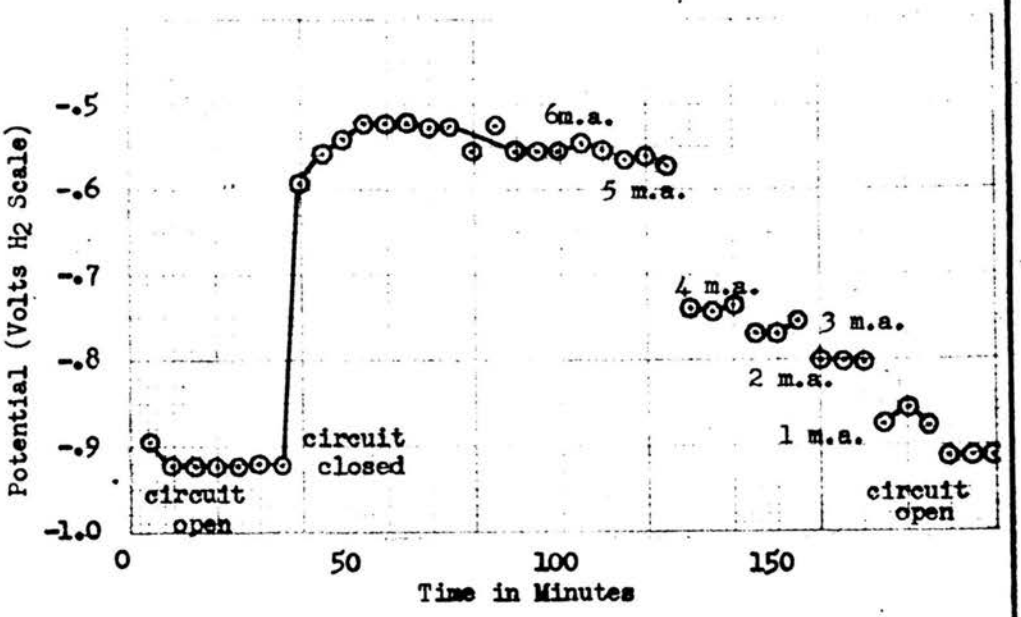
(iii) Results:

It was thought that the Battelle titanium being of higher purity than the Remington Arms titanium might give somewhat different results than those obtained with the Remington titanium, if the impurities were exerting some effort on the passivation phenomena. However, this was not the case, and results following the same general trend were obtained in both cases, and are listed in Tables LXI to LXVI. In all cases

the potential increased sharply when the switch was closed and the platinized platinum electrode, and milliameter put into the circuit. Then as the current density was decreased by increasing the external resistance, the potential readings became more negative. After the switch was opened again and the circuit was used only to measure the potential of the titanium electrode, the potential approximated the constant negative potential achieved before the switch was closed.

Plotting the potential, in volts corrected to the H_2 scale, against time, as shown in Figures 15 and 16, it is seen that the potentials rose sharply, becoming more positive, at the time the circuit was closed, then dropped, becoming more negative, at the times the current densities were decreased. The decrease of the current density with time is shown in Figure 17.

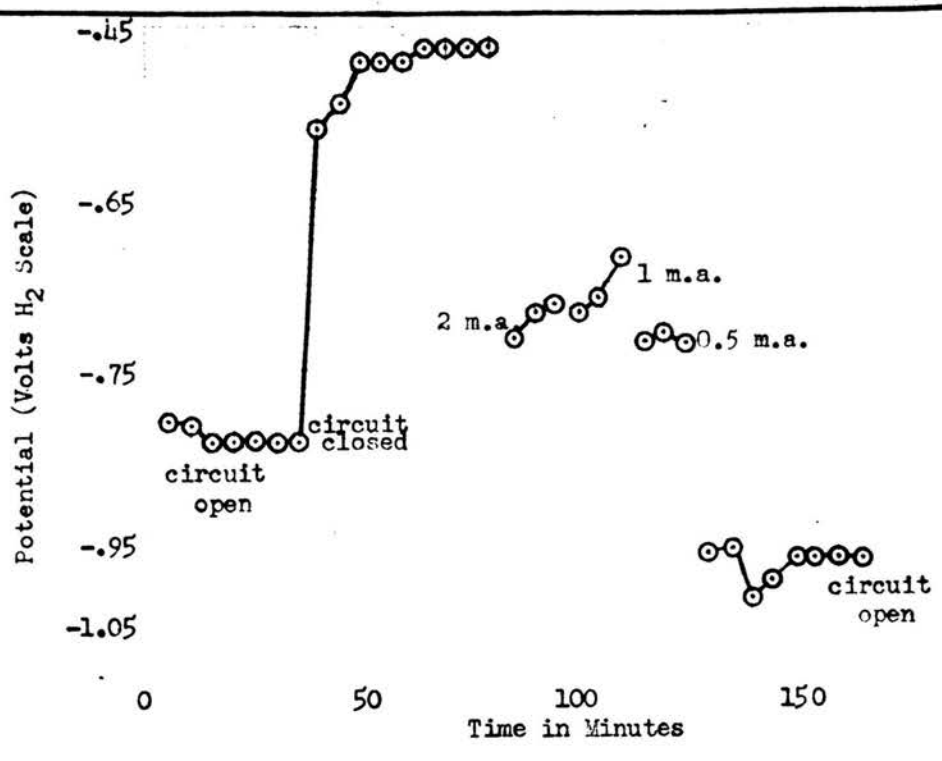
It was observed in every test that as soon as the acid saturated with NH_4F was put in the beaker and covered the electrodes, the titanium electrode very quickly became dark and passive. As the negative potential readings settled to a maximum constant value, a faint stream of H_2 was observed coming from the Ti electrode, and when the circuit was closed to include the platinized platinum electrode, a much stronger stream of H_2 was evolved from the Ti. After the circuit was opened again the Ti was either quite passive, or gave off only a faint stream of H_2. There was a dark surface film on the surface of the titanium after each run, which could be washed off with a stream of water leaving the titanium surface bright and shiny. No attempts were made to investigate the nature of the film.



4N HF plus 30 grams of NH_4F

Figure 15

Potential measurements of polarized Remington Arms Ti electrode with variable current in HF saturated with NH_4F electrolyte.



2N HF plus 30 grams of NH_4F

Figure 16

Potential measurements of polarized Battelle Ti electrode with variable current in HF saturated with NH_4F electrolyte.

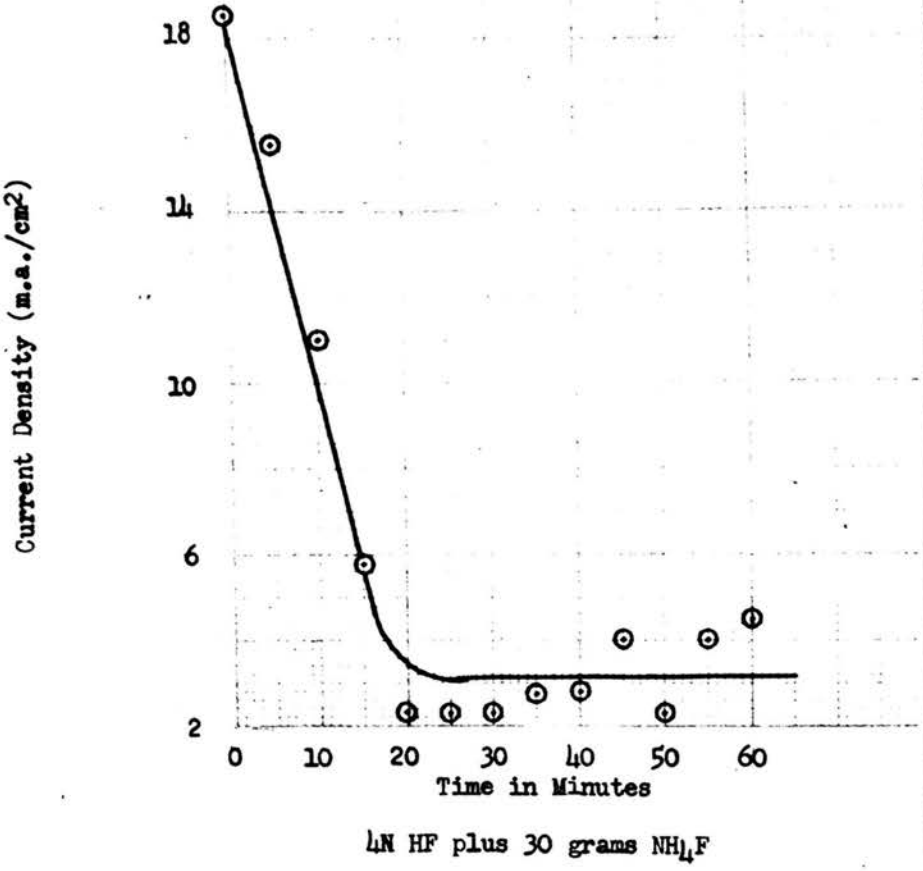


Figure 17

Current density decrease with time as passivating film forms on Remington Arms Ti electrode.

Table LXI

Potential and Current Density of Remington Arms Ti electrode in 1N HF plus 30 grams NH_4F

Time (Min.)	Potential H_2 scale	Time (Min.)	Current Density (M.A./cm^2)	Resistance
0	-1.011			
5	- .915			
10	- .974			
15	- .986			
20	- .985		(109.2 c.c. of 1N HF	
25	- .985		containing 30g. NH_4F)	
30	- .984			
35	- .984			
40	- .983			
45	- .982			
50	- .982			
55	- .981			
60	- .981			
65	- .981			
70	- .981			
75	- .979			
80	- .977			
85	- .977			
90	- .977			
95	- .977			
100	- .977			
6	- .537	5	3.5	0
11	- .537	10	3.0	
16	- .539	15	2.5	
21	- .557	20	2.5	
26	- .575	25	2.75	
31	- .557	30	2.5	
36	- .561	35	2.375	
41	- .576	40	2.5	
46	- .578	45	2.25	
51	- .587	50	2.5	
56	- .595	55	2.5	
61	- .601	60	2.5	
66	- .567	65	2.25	
71	- .605	70	2.75	

Table LXI Continued

5	- .857
10	- .848
15	- .908
20	- .911
25	- .911
30	- .911
35	- .911

Table LXII

Potential and Current Density of Remington Arms Ti electrode in 2N HF plus 30 g. NH_4F

Time (Min.)	Potential H_2 scale	Time (Min.)	Current Density (M.A./cm^2)	Resistance
0	-.933			
5	-.909			
10	-.941			
15	-.943		(113.5 c.c. of 2N HF	
20	-.945		containing 30g. NH_4F)	
25	-.945			
30	-.945			
35	-.945			
40	-.945			
45	-.945			
50	-.945			
55	-.945			
60	-.945			
65	-.945			
70	-.945			
75	-.945			
80	-.945			
85	-.945			
6	-.503	5	3.25	0
11	-.527	10	4.25	
16	-.541	15	4.3	
21	-.549	20	4.2	
26	-.558	25	4.05	
31	-.573	30	3.9	
36	-.581	35	4.5	
41	-.579	40	3.75	
46	-.579	45	4.0	
51	-.579	50	3.9	
56	-.581	55	4.0	
61	-.585	60	4.1	
66	-.591	65	4.1	

Table LXII Continued

5	-.925
10	-.915
15	-.911
20	-.909
25	-.909
30	-.909
35	-.909
40	-.909

Table LXIII

Potential and Current Density of Remington Arms Ti electrode in 4N HF plus 30 g. NH_4F

Time (Min.)	Potential H_2 scale	Time (Min.)	Current Density (M.A./cm^2)	Resistance (ohms)
0	-.834			
5	-.893			
10	-.920		(123.3 c.c. of 4N HF	
15	-.920		containing 30 g. NH_4F)	
20	-.918			
25	-.916			
30	-.916			
35	-.914			
6	-.594	5	15.5	0
11	-.562	10	11	
16	-.543	15	5.75	
21	-.526	20	2.375	
26	-.526	25	2.25	
31	-.524	30	2.25	
36	-.528	35	2.65	
41	-.528	40	2.75	
46	-.556	45	4.0	
51	-.524	50	2.3	
56	-.554	55	4.0	
61	-.559	60	4.5	
1	-.557	0	3	3
6	-.544	5	2.5	3
11	-.555	10	3	3
16	-.568	15	2.5	9
21	-.566	20	2.85	9
26	-.578	25	3.1	9
31	-.742	30	2.0	60
36	-.742	35	2.0	60
41	-.740	40	1.95	60
46	-.772	45	1.5	85
51	-.772	50	1.5	85
56	-.754	55	1.4	85

Table LXIII Continued

61	-.798	60	1.0	160
66	-.802	65	1.0	160
71	-.800	70	1.0	160
76	-.873	75	0.5	460
81	-.856	80	0.5	460
86	-.876	85	0.45	460

5	-.912
10	-.908
15	-.908
20	-.908

Table LXIV

Potential and Current Density of Battelle Ti electrode in 1N HF plus 30 g. NH_4F

Time (Min.)	Potential H_2 scale	Time (Min.)	Current Density (M.A./cm^2)	Resistance (ohms)
0	-1.107			
5	- .952			
10	-1.023		(109.2 c.c. of 1N HF	
15	-1.019		containing 30g. NH_4F)	
20	- .947			
25	- .839			
30	- .809			
35	- .813			
40	- .833			
45	- .831			
50	- .829			
55	- .829			
60	- .829			
6	- .485	5	21	0
11	- .441	10	15.5	
16	- .397	15	5	
21	- .397	20	4.4	
26	- .399	25	5	
31	- .379	30	3	
36	- .379	35	3	
41	- .379	40	3	
46	- .379	45	3	
1	- .717	0	4	200
6	- .687	5	3.5	200
11	- .676	10	3.2	200
16	- .683	15	1.8	400
21	- .665	20	2.0	400
26	- .619	25	1.6	400
31	- .719	30	1.0	1000
36	- .707	35	1.0	1000
41	- .718	40	1.0	1000

Table LXIV Continued

5	-.965
10	-.960
15	-1.009
20	-.993
25	-.972
30	-.969
35	-.965

Table LXV

Potential and Current Density of Battelle Ti electrode in 2N HF plus 30g. NH_4F

Time (Min.)	Potential H_2 scale	Time (Min.)	Current Density (M.A./cm^2)	Resistance (ohms)
0	-.949			
5	-1.008			
10	-.975		(113.5 c.c. of 2N HF	
15	-.883		containing 30g. NH_4F)	
20	-.859			
25	-.861			
30	-.861			
35	-.861			
40	-.855			
45	-.855			
50	-.855			
6	-.684	5	150	0
11	-.614	10	138	
16	-.585	15	124	
21	-.579	20	114	
26	-.575	25	110	
31	-.604	30	110	
36	-.515	35	80	
41	-.479	40	60	
46	-.446	45	24	
51	-.397	50	7	
56	-.395	55	6	
76	-.380	60	2	
1	-.681	0	1	600
6	-.631	5	1	600
11	-.617	10	1	600
16	-.699	15	.5	1800
21	-.705	20	.5	1800
26	-.709	25	.44	1800

Table LXV Continued

5	-.886
10	-.875
15	-.879
20	-.879
25	-.907
30	-.907
35	-.907

Table LXVI

Potential and Current Density of Battelle Ti electrode in 4N HF plus 30g. NH_4F

Time (Min.)	Potential H_2 scale	Time (Min.)	Current Density ($M.A./cm^2$)	Resistance (ohms)
0	-.886			
5	-.930			
10	-.871		(123.3 c.c. of 4N HF	
15	-.858		containing 30g. NH_4F)	
20	-.855			
25	-.855			
30	-.869			
35	-.879			
40	-.880			
45	-.912			
50	-.898			
55	-.896			
60	-.900			
6	-.801	5	274	0
11	-.781	10	256	
16	-.753	15	244	
21	-.757	20	232	
26	-.737	25	216	
31	-.671	30	174	
36	-.666	35	140	
41	-.586	40	22	
46	-.656	45	108	
51	-.570	50	16	
56	-.568	55	12	
76	-.778	75	12	
5	-.798			
10	-.812			
15	-.820			
20	-.834			
25	-.853			
30	-.853			
35	-.871			
40	-.871			
45	-.888			
50	-.888			

(iv) Conclusions:

From the results obtained it was seen that the negative potential was greatest during the self dissolution of the titanium, when the platinized platinum electrode was not in the circuit. Then when the platinum electrode was in the circuit, making the titanium the anode and the platinum the cathode, the negative potential increased and was highest when the current density was high. Thus, the anodic polarization forces the Ti to more noble potentials. However, this shift does not explain the high degree of passivation of the metal, as the most noble potentials obtained during polarization were about -0.4 volts, which is a sufficient potential to produce much stronger currents and rates of dissolution than observed. Consequently, the explanation of the passivation described does not lie in the more noble potential of the polarized Ti electrode.

The surface film observed, and noticed before when an excess of NH_4F was added to the corroding acid, did not adhere strongly to the titanium surface. On making the Ti electrode anodic the current apparently loosened the film, allowing it to be easily washed off the titanium, and leaving a new fresh, shiny surface. Such a film could not have a high resistance, but nevertheless an attempt was made to measure this resistance.

PART II

SECTION I

Resistance Measurements on Adding NH_4F to Various Acids, and of a Titanium Electrode in Hydrofluoric Acid.

As already mentioned, the second possible explanation of the passivation of the titanium might be due to the increased resistance of the acid mixture from the NH_4F additions, and the formation of a film of high resistance on the Ti electrode.

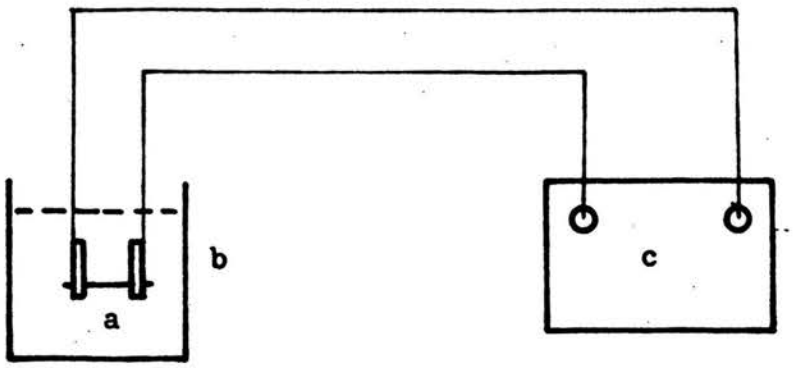
The resistance measurements are described in this chapter.

(i) Method and Apparatus:

The apparatus used consisted of a conductivity bridge, Type RC, and a Model 2A dip cell, both made by AMINCO. Two platinized platinum electrodes, a titanium electrode, variable resistance and milliammeter were the same as described previously.

(ii) Procedure:

For preliminary tests which determined the resistances when NH_4F was added in increasing amounts to 0.5N HCl, 1N HF, 1/10N H_2SO_4, 1/4N HF and H_2O in a beaker, the apparatus was connected as in Figure 18. The dip cell was inserted in the acid, and unmeasured amounts of NH_4F added, the solution stirred until the NH_4F was dissolved after each addition, then the resistance read from the conductivity bridge. This series of NH_4F additions was continued until the solution was super



a - dip cell, Pt electrodes
b - beaker
c - conductivity bridge

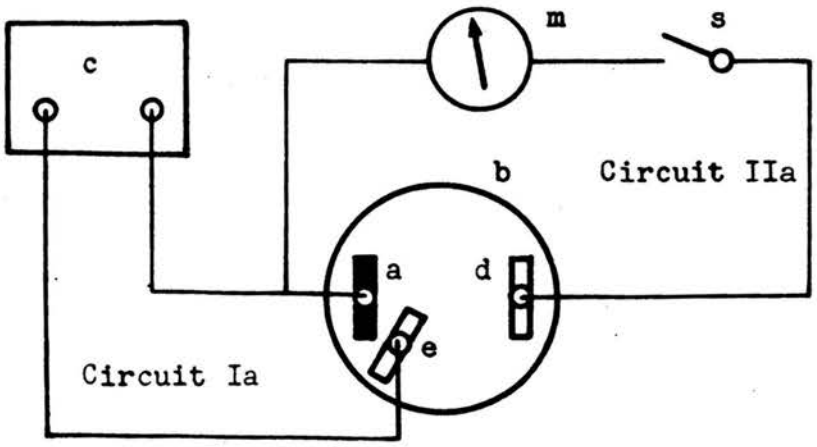
Figure 18

Apparatus for measuring the resistance of acids with added ammonium fluoride.

saturated with NH_4F. To measure the resistivity of the surface film on the Ti, the apparatus was then connected as shown in Figure 19. A great variety of dilute concentrations of HF were used as the electrolyte to find the acid concentration which would give the greatest rise in current density readings when the surface of the titanium electrode was scratched with a sharp pointed glass rod to break the surface film on the titanium. This HF concentration was found to be 1/40N HF. The two platinized platinum electrodes were adjusted as shown, so that there was as little interference as possible between them when only one or both were in the circuit.

The procedure followed was to close the switch and then open it quickly to get the maximum reading from the milliammeter, then read the resistance from the conductivity bridge. Next the switch was closed, and kept closed until the milliammeter readings had dropped down to a minimum, then the switch was opened and the resistance read. In this way only the resistance of circuit I was taken, not circuit II as well, which would happen if resistance readings were taken with the switch closed. All resistance readings were taken only with the switch open. As there was no way of knowing in this casewhat the constant was of the improvised dip cell, all the resistance results obtained were only relative to each other, for a qualitative orientation CO_2 gas was bubbled into the acid to see if saturating the solution with CO_2 instead of O_2 picked up from the air would have any effect on the resistance measurements.

Next, an external E. M. F. in the form of a 12 volt wet cell,



a - Ti electrode
b - beaker
c - conductivity bridge
d - Pt electrode
e - Pt electrode
m - milliammeter
s - switch

Figure 19

Apparatus for measuring the resistance of the surface of a Ti electrode.

and a variable resistance were attached to circuit II, and connected as shown in Figure 20. The procedure followed now was to close switch I, open switch II and read the resistance; open switch I, close switch II and let the current drop to a minimum; then open switch II, close switch I and read the resistance. The variable resistance was adjusted to try and find the current density where the current would drop to its lowest point, and the 12 volt wet cell put in the circuit to impress an E. M. F. on circuit II and make sure the platinized platinum electrode was the cathode of the electrolytic cell, and also well saturated with hydrogen.

(iii) Calculations:

The resistance results obtained for the preliminary tests were all corrected to 18° C (generally used as a reference point) by the method described in the Operating Manual of the AMINCO conductivity bridge for correction to 18° C.

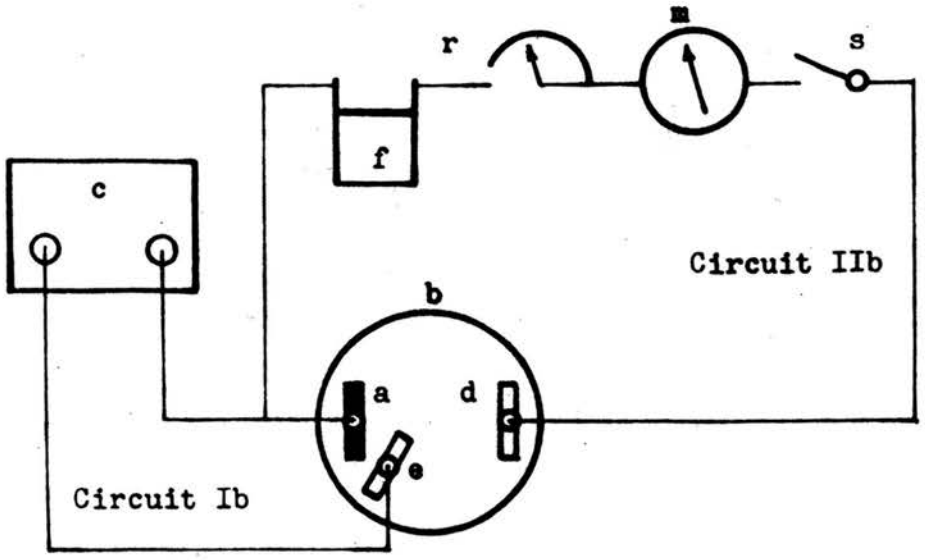
Using the data from Table LXVII with 0.5N HCl plus NH_4F as an example:

$$R_{18} = Rt\ (1 + .02\Delta t)$$

where R_{18} = measured resistance corrected to 18° C
Rt = measured resistance at temperature of test
Δt = difference in temperature between 18° C and temperature of test measurement.

Rt = 0.81 ohms
$\Delta t = (21.4-18) = 3.4°$ C
$R_{18} = 0.81(1 + .02 \times 3.4) = 0.81 \times 1.068$
Dip cell constant = 0.102

$$R_{18} = \frac{0.81 \times 1.068}{0.102} = 8.48 \text{ ohms}$$



a - Ti electrode
b - beaker
c - conductivity bridge
d - Pt electrode
e - Pt electrode
f - battery
r - variable resistance
m - milliammeter
s - switch

Figure 20

Apparatus for measuring the resistance of the surface of a Ti electrode, with impressed voltage.

(iv) Results:

From the preliminary tests made by adding NH_4F in increasing amounts to 1N HF, 1/4N HF, 1/2N HCl, 1/10N H_2SO_4, and H_2O, one feature stood out, and that was that the resistance dropped considerably when NH_4F was dissolved in the acids. The results are given in Table LXVII.

The resistance measurements with the titanium electrode in 1/40 N HF were on the whole rather inconclusive. Usually, the titanium electrode had a slightly greater resistance after the anodic polarization, along the order of 1365 ohms after the anodic polarization as against 1360 ohms before. There seemed to be no appreciable change in the resistance readings when read before and after the maximum current readings, and it was only after the low steady minimum current had been reached and the anode polarized that there was the slight rise in resistance. The same general trend followed when CO_2 was bubbled into the solution.

With the 12 volt wet cell and variable resistance in the circuit the results remained unchanged. When the voltage of the cell was increased by 2 volt steps from 2 volts to 8 volts the current increased, but in no definite ratio. However, when the leads were reversed making the Ti the cathode instead of the anode, then the current increased in a direct proportion to the amount of voltage applied.

When the Ti surface was scratched to expose a fresh surface of Ti, the current would rise slightly in most instances.

Table LXVII

Resistance Measurements on adding NH_4F to various acids.

NH_4F	Acid	Temp. (°C)	Resistance (Ohms 18°C)	Acid	Temp. (°C)	Resistance (Ohms 18°C)
0	1N HF	21.1	465	1/4N HF	21.0	118.65
			132			15.58
increasing			87			8.62
additions			75			6.75
			67			6.76
			63			
0	1/2N HCl	21.4	8.48	1/10N H_2SO_4	21.3	45.5
			8.90			12.18
			6.81			7.42
increasing			6.28			6.79
additions			6.18			6.37
0	H_2O	22.7	147952.56			
			17.9			
increasing			10.6			
additions			8.25			
			7.4			

(v) Conclusions:

The rapid drop in the current to a low, steady value shows that the titanium electrode is going passive quickly, and some sort of a protective film must form on the surface of the titanium. That this protective film slows down the current is illustrated by scratching the surface of the titanium to expose a fresh surface, after which the current rises, then drops again as the film once more covers the freshly exposed surface.

A puzzling feature though, was that the resistance of the titanium electrode was not raised appreciably by this film forming on it. However, it is very possible that the resistance of the film drops very quickly as soon as the anodic polarizing current is interrupted in order to measure the resistance. Unfortunately, resistance measurements with the polarizing current on could not be made because of experimental difficulties, (the a.c. of the resistivity bridge being out of the range of the milliammeter and variable resistance).

So, the experiments showed that the passivation of titanium in the presence of large amounts of NH_4F may be partially explained by the formation on the titanium of films with greater resistivity than those formed in pure, dilute HF. However, the presence of a bright Ti surface in the presence of NH_4F, and its very negative potential (-.922 volts), shows that in this case the formation of a new kind of film is only secondary.

PART II

SECTION J

The Hydrogen Overvoltage on Platinum and Copper in Hydrofluoric Acid Solutions with Ammonium Fluoride or Agar-Agar.

The third possible explanation for the passivity of titanium may be connected with an overvoltage phenomena, as the overvoltage of the local cathodes in the Ti electrode, as well as the overvoltage of the Ti itself, may rise in the presence of large amounts of NH_4F.

To test this probability, overvoltage measurements were made on platinum and copper in the presence of NH_4F, and of agar-agar.

Evans 4) states that a cathode metal of low overvoltage will allow far more corrosion at the anode than a metal with high overvoltage, and that this increase in corrosion rate will cease to be proportional

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4) Evans, U. R., op. cit. p. 49, 503

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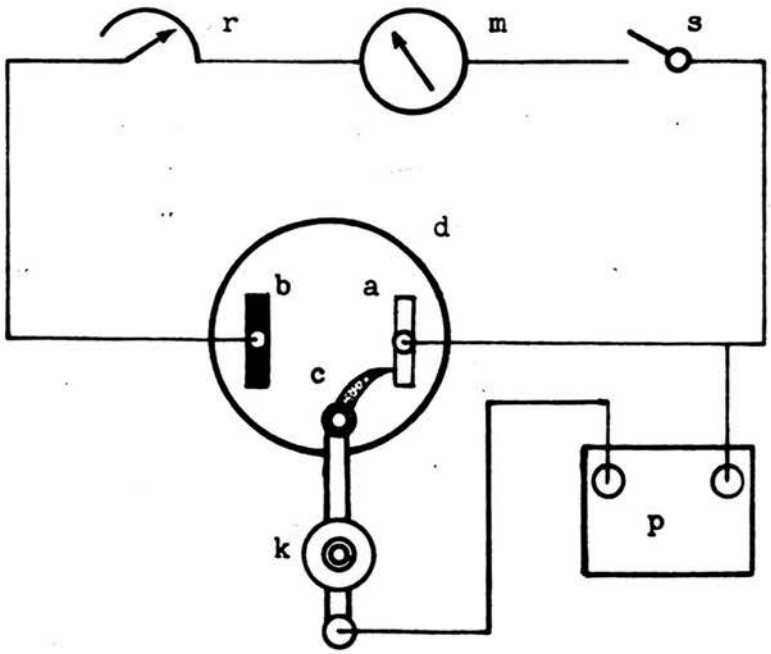
to the cathodic area if the resistance is too high, the cathode/anode ratio too great, or if there is appreciable anodic polarization.

(i) Method and Apparatus:

The apparatus was similar to that used to measure the potential of the titanium electrode, except in this case only the potential of the platinized platinum electrode was measured. A schematic diagram of



a - Pt electrode
b - Ti electrode
c - capillary tube from calomel cell
d - beaker
k - calomel cell
p - potentiometer
m - milliammeter
r - variable resistance
s - switch

Figure 21

Apparatus for overvoltage measurements.

the circuit used is shown in Figure 21. The overvoltage measurements were performed by the direct method [11], taking the potential of the

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11) Prutton, C. F., and Maron, S. E., Fundamental Principles of Physical Chemistry, MacMillan Co., New York, p. 586, (1947)

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cathode when current is passing.

(ii) Procedure:

A preliminary test was made by adding NH_4F in 3 gram increments to 60 c.c. of 0.5N HF, adjusting the variable resistance to give the same current after each NH_4F addition had been dissolved, and reading the potential of the platinized platinum electrode.

Next, 56 c.c. of 4N HF was used as the electrolyte, and NH_4F added in 3 gram increments. During this series of tests the variable resistance was manipulated to give as great a range of current readings as possible for each mixture of 4N HF plus NH_4F addition and the potential read for each. The potential of the platinized platinum electrode was recorded at each of these current reading points.

A similar test was conducted using a copper electrode coated with a copper sponge in place of the platinized platinum. The copper electrode was covered with a copper sponge by placing the copper electrode connected as a cathode, and a platinized platinum electrode as the anode in a solution of $Cu\ SO_4$, and applying a high current density. The coated copper electrode was then left in distilled water for one

hour to wash out any entrapped $CuSO_4$ solution.

As the rate of dissolution of Ti decreased in the presence of agar-agar added to HF solutions (p.87a), a similar series of tests were made with the platinized platinum and copper electrodes, adding 2% agar-agar in 2 c.c. increments instead of the NH_4F.

The overvoltage of the platinized platinum and copper electrodes was then plotted versus to $\log_{10}$ of the current density applied.

(iii) Calculations:

The hydrogen overvoltage of the platinum and copper electrodes was calculated according to the expression

$$N = -(a + b \log_{10} i) \qquad (12)$$

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(12) Tafel, J., Zeitsch Phys. Chem., 50, 645, (1905)

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where N = the hydrogen overvoltage in volts or m.v.
i = the current density in m.a./cm^2
a & b = constants.

According to this equation a plot of N against $\log_{10} i$ should be linear, with the slope of the line "b", and the y intercept "a".

As an illustration, using the data from Table LXIX and Figure 24, with 0 grams of NH_4F added.

i = 1 , 10 , 20 , 30 , 40 milliamps
$\log_{10}$ i = 0.0, 1.00 ,1.301 ,1.477 , 1.602
a = 100 (the y intercept of plotting N (observed) against $\log_{10} i$, as shown in Figure 24)

$$b = \frac{N-a}{\log_{10} i} = \frac{115-100}{1.00} = 15.0$$

$$\frac{122-100}{\log_{10} i} = \frac{22}{1.301} = 16.9$$

$$\frac{132-100}{\log_{10} i} = \frac{32}{1.477} = 21.7$$

$$\frac{135-100}{\log_{10} i} = \frac{35}{1.602} = 21.9$$

$$\text{Average } b = \frac{(15 + 16.9 + 21.7 + 21.9)}{4}$$

$$= 18.9, \text{ (or 0.0189 volts/log}_{10} \text{ amps.)}$$

This particular equation is therefore,

$$N = -(100 + 18.9 \log i)$$

and the calculated overvoltages are,

i	N(calculated)	N(observed) (Table LXIX)	Δ N
10	-118.9	-115	-3.9
20	-124.7	-122	-2.7
30	-127.9	-132	+4.1
40	-130.3	-135	+4.7

The "b" value used in these calculations is 1000 times greater than usual, as the current is expressed in milliamps instead of amperes (see example).

The difference Δ N shows that the curve obtained is not quite logarithmic, but expression (12) can be used in order to compare the different results.

(iv) Results:

The results from the preliminary test of adding NH_4F in 3 gram increments to a 0.5N HF electrolyte and reading the potential of the platinum cathode after each addition was in solution, as given in Table LXVIII, showed that the potential becomes increasingly more negative in proportion to the amount of NH_4F added.

The results from adding NH_4F in increasing increments to an electrolyte of 4N HF, recording the potential readings of the platinum and copper cathodes for each increment, and calculating the hydrogen overvoltage, are given in Tables LXIX to LXXII. In Figure 22 the potentials corrected to the H_2 scale at 25° is plotted against the current density, and in Figure 23 the potentials are plotted against $\log_{10}$ current density. Figure 24, and Table LXXIII show respectively the current density plotted against corrected potential, and potential measurements of the platinum electrode with very low current density.

The results of the tests when 2% agar-agar was added in increments to the 4N HF electrolyte are given in Tables LXXIV to LXXVII, and the corrected potentials of the electrodes plotted against $\log_{10}$ current density in Figure 25.

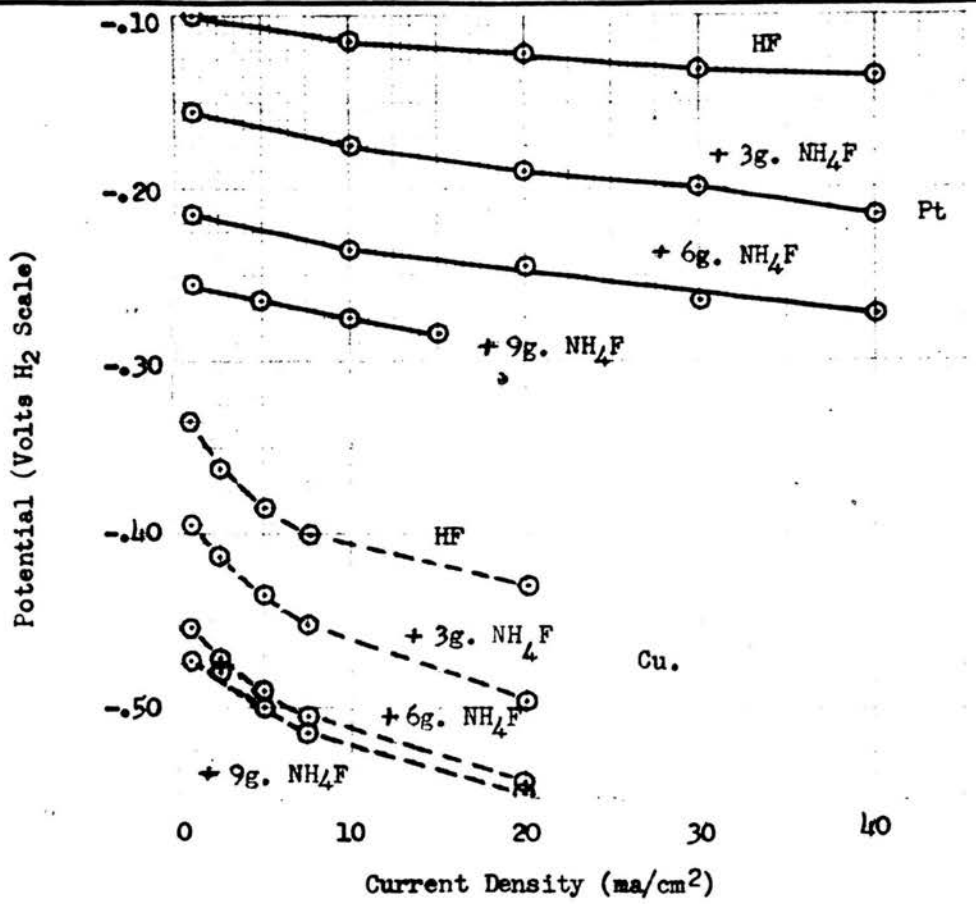

Figure 22

Potential (overvoltage) measurements of Pt and Cu electrodes in HF plus NH_4F.

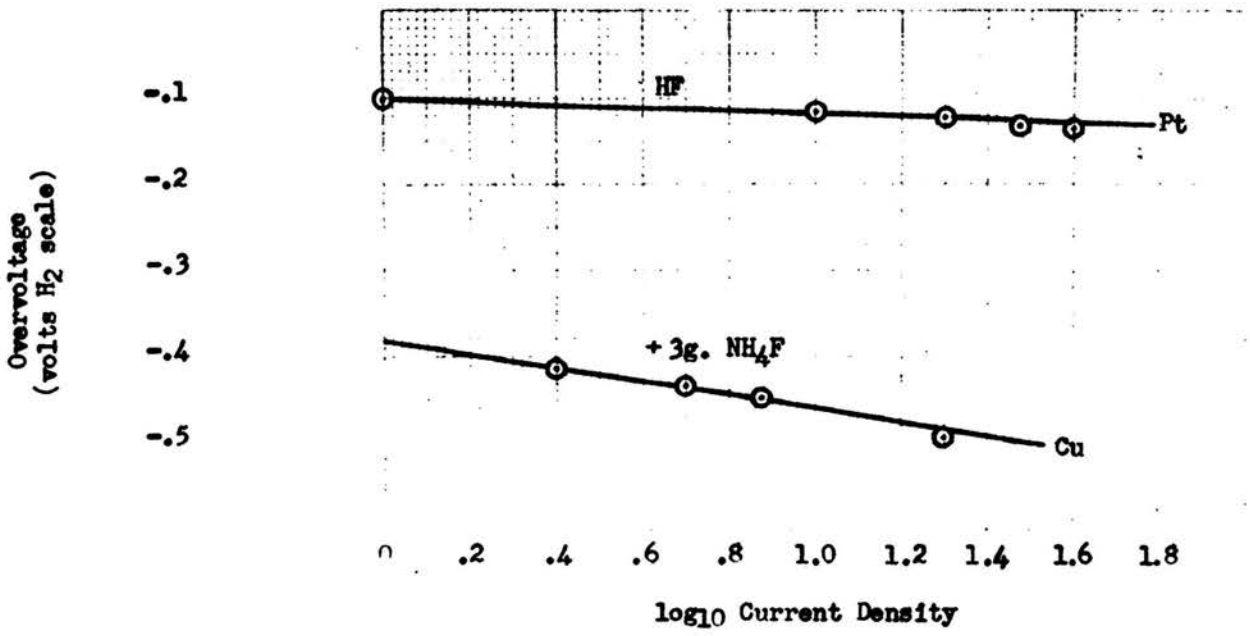

Figure 23

Straight line according to equation $N = -(a + b \log_{10} i)$ compared to experimental points.

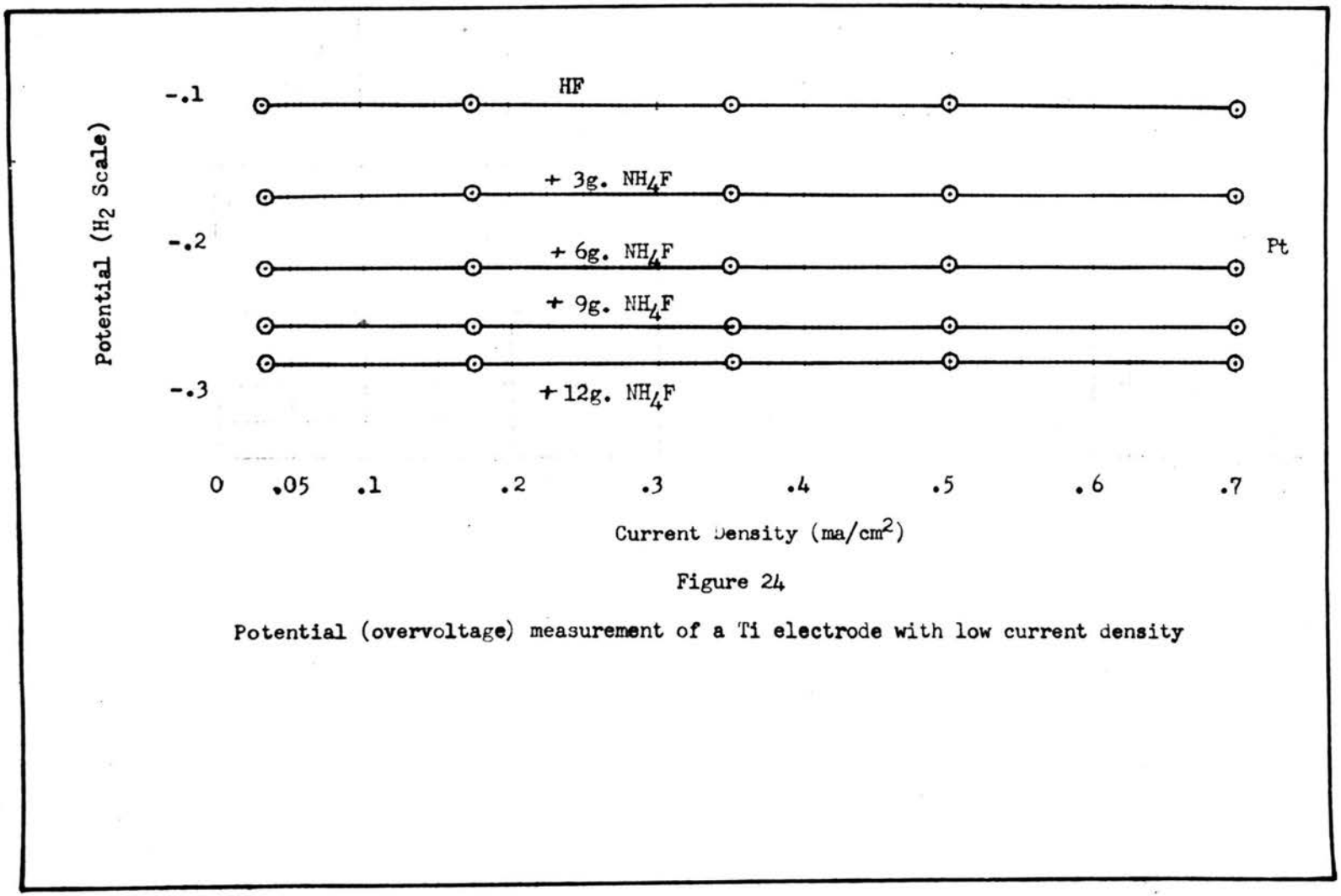

Figure 24

Potential (overvoltage) measurement of a Ti electrode with low current density

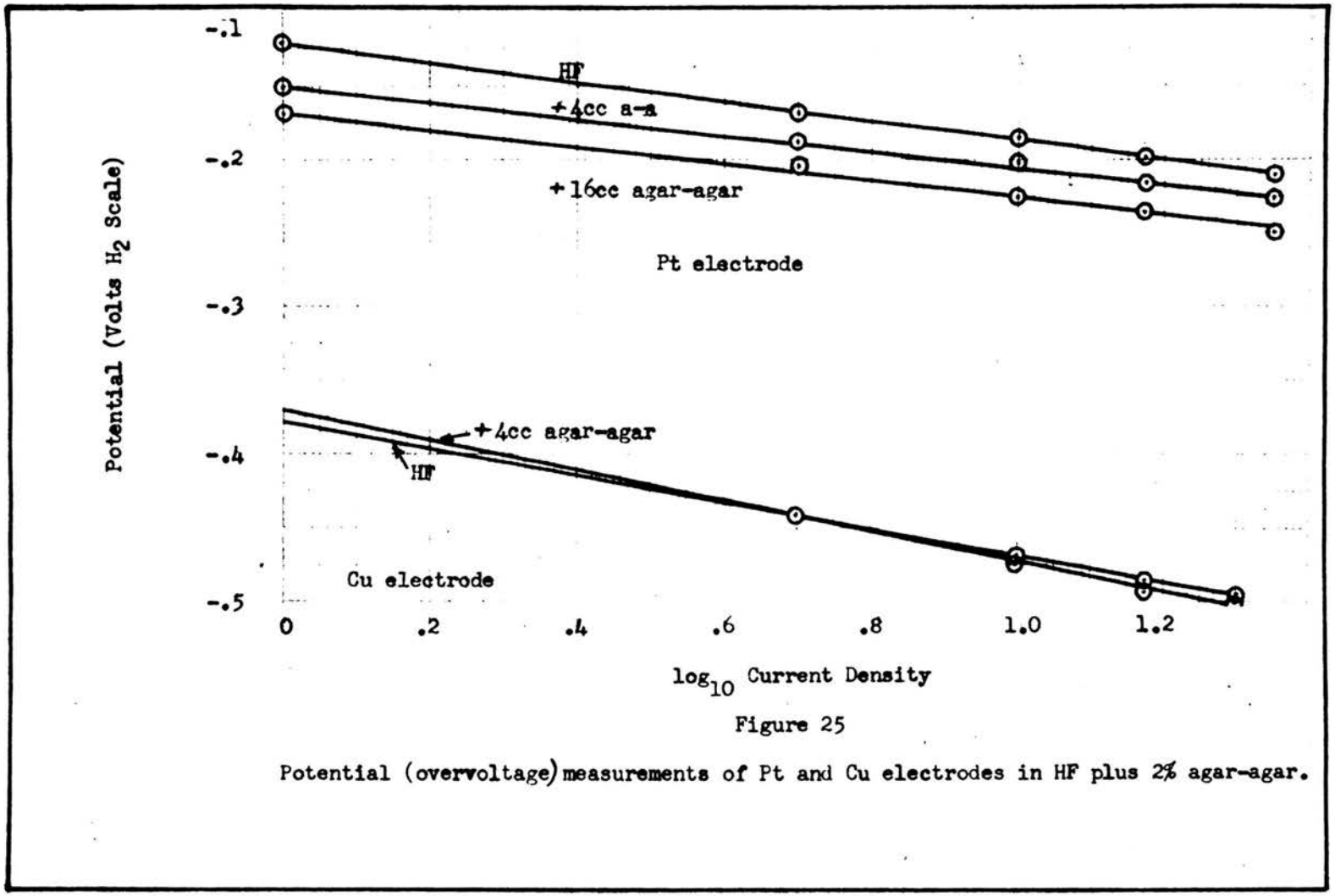

Figure 25

Potential (overvoltage) measurements of Pt and Cu electrodes in HF plus 2% agar-agar.

Table LXVIII

Hydrogen overvoltage of a platinized platinum electrode in 60 c.c. of 0.5N HF plus NH_4F, with a constant current density.

Overvoltage (H_2 scale)	Current Density (m.a./cm^2)	NH_4F (grams)
-.145	1	0
-.268	1	3
-.297	1	6
-.318	1	9
-.335	1	12
-.347	1	15
-.352	1	18
-.361	1	24
-.365	½	27
-.371	½	30

Table LXIX

Potential (overvoltage) measurements of a platinized platinum electrode in 56 c.c. of 4N HF plus NH_4F, with variable current density.

NH_4F (grams)	i in m.a./cm^2 1	10	20	30	40
	Overvoltage (H_2 scale)				
0	-.100	-.115	-.122	-.132	-.135
0	-.089	-.127	-.161	-.175	-.191
3	-.156	-.174	-.189	-.200	-.213
6	-.213	-.235	-.245	-.263	-.271
9	-.255	-.275	-.283		

Table LXX

Hydrogen overvoltage of platinized platinum electrode in 56 c.c. of 4N HF plus NH_4F

i (m.a./cm^2)	log i	a	b	N (calc.)	N (obs.)	Δ N	NH_4F (grams)
10	1.00	100	18.9	-118.9	-115	-3.9	0
20	1.301			-124.7	-122	-2.7	
30	1.477			-127.9	-132	4.1	
40	1.602			-130.3	-135	4.7	
10	1.00	89	52.3	-141.3	-127	-14.3	0
20	1.301			-157.0	-161	4.0	
30	1.477			-166.2	-175	8.8	
40	1.602			-172.6	-191	18.8	
10	1.00	156	26.95	-183	-174	-9.0	3
20	1.301			-189.8	-189	-0.8	
30	1.477			-194.1	-200	5.9	
40	1.602			-197.6	-213	15.4	
10	1.00	213	30.05	-243	-235	-8.0	6
20	1.301			-252	-245	-7.0	
30	1.477			-257.3	-263	5.7	
40	1.602			-261	-271	10.0	
10	1.00	255	21.9	-276.9	-275	-1.9	9
15	1.176			-280.8	-283	2.2	

Table LXXI

Potential (overvoltage) measurements of a copper electrode in 56 c.c. of 4N HF plus NH_4F, with variable current density.

NH_4F (grams)	i in m.a./cm^2			
	2.5	5	7.5	20
	Overvoltage (H_2 scale)			
0	-.330	-.368	-.366	-.412
0	-.364	-.385	-.400	-.430
3	-.413	-.436	-.452	-.496
6	-.472	-.492	-.503	-.544
9	-.478	-.499	-.511	-.549

Table LXXII

Hydrogen overvoltage of copper electrode in 56 c.c. of 4N HF plus NH_4F

i C.D. (m.a./cm^2)	log i	a	b	N (calc.)	N (obs.)	Δ N	NH_4F (grams)
2.5	.398	280	112.5	-324.8	-330	5.2	0
5	.699			-342.2	-368	25.8	
7.5	.875			-378.4	-366	-12.4	
20	1.301			-426.1	-412	-14.1	
2.5	.398	335	73.2	-364.2	-364	-0.2	0
5	.699			-386.2	-385	-1.2	
7.5	.875			-399	-400	1	
20	1.301			-430.1	-430	-0.1	
2.5	.398	380	83.65	-413.3	-413	-0.3	3
5	.699			-438.5	-436	-2.5	
7.5	.875			-453.2	-452	-1.2	
20	1.301			-488.7	-496	7.3	
2.5	.398	443	72.55	-471.9	-472	0.1	6
5	.699			-493.8	-492	-1.8	
7.5	.875			-506.4	-503	-3.4	
20	1.301			-537.3	-544	6.7	
2.5	.398	455	64.2	-480.6	-478	-2.6	9
5	.699			-499.8	-499	-0.8	
7.5	.875			-511.2	-511	-0.2	
20	1.301			-538.4	-549	10.6	

Table LXXIII

Potential (overvoltage) measurements of platinized platinum electrode in 56 c.c. of 4N HF plus NH_4F with low current density.

NH_4F (grams)	i in m.a./cm^2				
	.0325	.175	.35	.5	.7
	Overvoltage (H_2 scale)				
0	-.109	-.109	-.109	-.113	-.112
3	-.172	-.171	-.172	-.172	-.172
6	-.221	-.221	-.221	-.221	-.221
9	-.262	-.262	-.262	-.262	-.262
12	-.286	-.286	-.286	-.286	-.286

Table LXXIV

Potential (overvoltage) measurements of platinized platinum in 56 c.c. 4N HF plus 2% agar-agar, with variable current density.

2% agar-agar (c.c.)	i in m.a./cm^2 5	10	15	22.5
	Overvoltage (H_2 scale)			
0	-.184	-.204	-.214	-.221
2	-.185	-.206	-.221	-.228
4	-.186	-.209	-.221	-.231
6	-.194	-.218	-.231	-.244
8	-.200	-.220	-.236	-.249
12	-.199	-.222	-.234	-.249
16	-.201	-.227	-.238	-.252

Table LXXV

Hydrogen overvoltage of platinized platinum electrode in 56 c.c. of 4N HF plus 2% agar-agar.

i C. D. ($m.a./cm^2$)	log i	a	b	N (calc.)	N (obs.)	Δ N	2% Agar-Agar (c.c.)
5	.699	133	69.5	-181.6	-184	2.4	0
10	1.00			-202.5	-204	1.5	
15	1.176			-214.8	-214	-0.8	
22.5	1.352			-226.8	-221	-5.8	
5	.699	136	70.1	-185	-185	0.0	2
10	1.00			-206	-206	0.0	
15	1.176			-218.4	-221	2.6	
22.5	1.352			-230.7	-228	-2.7	
5	.699	144	63.75	-188.6	-186	-2.6	4
10	1.00			-207.8	-209	1.2	
15	1.176			-218.8	-221	2.2	
22.5	1.352			-230	-231	1.0	
5	.699	148	69.35	-196.5	-194	-2.5	6
10	1.00			-217.4	-218	0.6	
15	1.176			-229.5	-231	1.5	
22.5	1.352			-241.6	-244	2.4	
5	.699	155	66.95	-201.8	-200	-1.8	8
10	1.00			-221.95	-220	-1.95	
15	1.176			-233.7	-236	2.3	
22.5	1.352			-245.4	-249	3.6	
5	.699	159	62.65	-202.8	-199	-3.8	12
10	1.00			-221.65	-222	0.35	
15	1.176			-232.7	-234	1.3	
22.5	1.352			-243.6	-249	5.4	
5	.699	162	63.0	-206.1	-201	-5.1	16
10	1.00			-225	-227	2.0	
15	1.176			-236.2	-238	1.8	
22.5	1.352			-247.1	-252	4.9	

Table LXXVI

Potential (overvoltage) measurements of copper electrode in 56 c.c. of 4N HF plus 2% agar-agar, with variable current density.

2% agar-agar (c.c.)	i in m.a./cm^2 5	10	15	19.5
	Overvoltage (H_2 scale)			
0	-.443	-.468	-.485	-.495
2	-.443	-.473	-.491	-.501
4	-.443	-.475	-.493	-.504
6	-.442	-.473	-.489	-.501
8	-.437	-.473	-.486	-.502
12	-.433	-.461	-.484	-.497
16	-.426	-.463	-.483	-.489

Table LXXVII

Hydrogen overvoltage of copper electrode in 56 c.c. of 4N HF plus 2% agar-agar.

i C. D. (m.a./cm^2)	log i	a	b	N (calc.)	N (obs.)	Δ N	2% Agar-Agar (c.c.)
5	.699	379	90.1	-442	-443	1	0
10	1.00			-469.1	-468	-1.1	
15	1.176			-485	-485	0.0	
19.5	1.29			-495.2	-495	-0.2	
5	.699	368	104.9	-441.4	-443	1.6	2
10	1.00			-472.9	-473	0.1	
15	1.176			-491.3	-491	-0.3	
19.5	1.29			-503.3	-501	-2.3	
5	.699	367	107.5	-442.3	-443	0.7	4
10	1.00			-474.5	-475	0.5	
15	1.176			-493.2	-493	-0.2	
19.5	1.29			-505.7	-504	-1.7	
5	.699	374	98.1	-442.6	-442	0.4	6
10	1.00			-472.1	-473	0.9	
15	1.176			-589.3	-489	-0.3	
19.5	1.29			-500.7	-501	0.3	
5	.699	358	112.5	-436.7	-437	0.3	8
10	1.00			-470.5	-473	2.5	
15	1.176			-480.2	-486	5.8	
19.5	1.29			-503.1	-502	-1.1	
5	.699	348	117	-429.8	-433	3.2	12
10	1.00			-465	-461	-4.0	
15	1.176			-485.5	-484	-1.5	
18.5	1.276			-496.1	-477	0.9	
5	.699	344	118	-426.6	-426	-0.6	16
10	1.00			-462	-463	1.0	
15	1.176			-482.8	-483	0.2	
17.5	1.243			-490.8	-489	-1.8	

(v) Conclusions:

The logarithmic relation between overvoltage N and current density i was first discovered by Tafel [12], and this relationship between current density and hydrogen overvoltage given further study by many later investigators. Among the foremost of these investigators is Knobel [13], with his co-workers. According to these various studies,

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13) Knobel, M., Caplan, C. and Eiseman, M., The Effect of Current Density on Overvoltage, Trans. Amer. Electrochem. Soc. 43, 55, (1923)

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hydrogen overvoltage is a function of current density, and in this instance it is also strongly effected by additions to the electrolyte. The plots of N against $\log_{10} i$ were nearly linear, as they should be to be represented by the equation $N = -(a + b \log_{10} i)$, and the differences between N(observed) and N(calculated) were small and practically self cancelling.

All the measurements made in this chapter show definitely that the hydrogen overvoltage of metals platinum and copper increases with the increasing concentration of NH_4F in the electrolyte. This is characterized by the increase of the constant "a" (Figure 23, Table LXX), while the slope constant "b" is not so strongly effected. Even at low current densities (Figure 24) "a" increases strongly and steadily. The overvoltage is the only quality which changes with increasing NH_4F in such a manner that it causes a decrease in the rate of dissolution of Ti. So it can be concluded that the passivity of

Ti, in solutions containing NH_4F in large amounts, is caused by the increasing hydrogen overvoltage of the cathodic impurities, consisting of metals more noble than Ti, on the titanium surface. It may be that they hydrogen overvoltage of Ti itself increases considerably with increasing NH_4F , but this was not checked.

A further example in favour of this theory of passivation due to overvoltage, were similar experiments with agar-agar additions to the electrolyte. In Chapter E it was shown that the rate of dissolution of Ti decreased 17.2% when 10 c.c. of 2% agar-agar was added to 1N HF in which Ti was dissolving. Figure 25 clearly shows that the overvoltage on platinum and copper is increased (see "a" and "b" constants Tables LXXV and LXXVII) with agar-agar additions, although not so strongly as in the case of NH_4F additions. Nevertheless, the two are roughly parallel, with the cathodic impurities on the Ti surface absorbing the agar-agar molecules,and the overvoltage increasing on these spots. The EMF of the local cells decreases, and with it the rate of dissolution.

CHAPTER IV

Discussions and Conclusions

PART I

The Rates of Dissolution and the Mass Action Law

The condition of equilibrium, at a given temperature, in the case of a balanced or reversible reaction can be obtained by applying the law of mass action. This law states that the velocity of a reaction at constant temperature is proportional to the produce of the cencentrations of the reacting substances, the concentrations being expressed in gram-molecules per litre.

On applying the law of mass action to determine the condition of equilibrium in the case of a reversible reaction taking place in an homogeneous system at constant temperature, we get for the general equation

$$A + B \rightleftharpoons C + D$$

The velocity of the reaction A + B is equal to $k_1[A]x[B]$, and the velocity of the reverse reaction C + D is equal to k_2 [C] x [D], where k_1 and k_2 are constants known as velocity coefficients. When the conditions are such that the velocities of these two reactions are identical, a state of equilibrium results, and $k_1[A]x[B]$ is equal to $K_2[C]x[D]$, from which it follows

$$\frac{[C]x[D]}{[A]x[B]} = \frac{k_1}{k_2} = K$$

K being known as the equilibrium constant of the particular reaction.

This law of mass action was applied to the equation

$$NH_4F + H_2SO_4 \rightleftharpoons (NH_4)HSO_4 + HF \qquad (2)$$

to test the validity of the assumption, which was made for the investigations of rates of dissolution of titanium, that this reaction reaches a state of equilibrium, and the NH_4F added to H_2SO_4 forms HF.

A comparison was made of corresponding rates of dissolution of titanium in HF alone, and in NH_4F (in N) dissolved in 4N H_2SO_4 and 2N H_2SO_4, (Figures 4 and 6) to determine the actual normality of the NH_4F added in relation to pure HF. The rates of dissolution in HF alone were according to Straumanis and Chen [2]. As an example, from

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2) Straumanis, M. E., and Chen, P. C. op. cit. p. 239

Figure 4, the rate of dissolution of Ti in 1.25N HF is 690 mm^3/cm^2min., which is also the rate of dissolution of Ti in 1.62N NH_4F plus 4N H_2SO_4. The results of this comparison are listed in Table LXXVIII.

Table LXXVIII

The comparison of equal rates of dissolution of Ti in HF and 4N H_2SO_4 plus NH_4F, and 2N H_2SO_4 plus NH_4F

N HF	N NH_4F + 4N H_2SO_4	Rates of Dissolution (mm^3/cm^2-min.)
.35	.395	270
.75	.895	460
.85	1.03	505
1.0	1.25	588
1.15	1.47	647
1.25	1.62	690
1.35	1.75	735
1.5	1.98	810

N HF	N NH_4F + 2N H_2SO_4	Rates of Dissolution (mm^3/cm^2-min.)
.2	.5	183
.3	.63	234
.35	.70	259
.4	.77	284
.45	.84	311
.5	.91	332
.55	.98	360

These values were substituted in the equation

$$NH_4F + H_2SO_4 \rightleftharpoons (NH_4)HSO_4 + HF \qquad (2)$$

to find the equilibrium constant K.

$$K = \frac{[HF][(NH_4)HSO_4]}{[NH_4F][H_2SO_4]}$$

Using as an example 1.15N HF, compared to 1.47N NH_4F plus 4N H_2SO_4, (Table LXXVIII), and assuming that the actual concentration of the liberated HF is 1.15N, originating from 1.47N NH_4F. The concentration of H_2SO_4 is then 4-1.15N, and the value for the equilibrium constant is

$$K = \frac{[1.15][1.15]}{[1.47-1.15][4-1.15]} = \frac{1.3225}{0.912} = 1.45$$

The calculated equilibrium constants K are listed in Table LXXIX. In the case of 4N H_2SO_4, the K values give a fairly good consistency, showing that the concentration of HF liberated is in agreement with the requirements of the law of mass action. However, while one would also expect the same equilibrium constant for 2N H_2SO_4, this is not the case.

To test the accuracy of the calculated average K values (Table LXXIX), these values along with the known concentrations of NH_4F and H_2SO_4 (Table LXXVIII) were put into the expression

$$K = \frac{[HF][(NH_4)HSO_4]}{[NH_4F][H_2SO_4]}$$

to find the concentrations of HF corresponding to the concentrations of NH_4F plus 2N and 4N H_2SO_4, which were used to compute the average K values.

Table LXXIX

Calculated equilibrium constants K

N HF	N NH_4F + 4N H_2SO_4	K
.35	.395	(.75)
.75	.895	1.19
.85	1.03	1.27
1.0	1.25	1.33
1.15	1.47	1.45
1.25	1.62	1.54
1.35	1.75	1.72
1.5	1.98	1.88
		Average 1.39

N HF	N NH_4F + 2N H_2SO_4	K
.2	.5	.074
.3	.63	.160
.35	.7	.212
.4	.77	.270
.45	.84	.335
.5	.91	.406
.55	.98	.485
		Average 0.269

As an example, using data from Table LXXVIII where N NH_4F plus 4N H_2SO_4 is 1.03N, and from Table LXXIX where the average K value is 1.39 for NH_4F plus 4N H_2SO_4

$$K = \frac{x \times x}{(NH_4F-x)(H_2SO_4-x)}$$

$$1.39 = \frac{x^2}{(1.03-x)(4-x)}$$

$$1.39 = \frac{x^2}{4.12-5.03x+x^2}$$

$$0.39x^2-6.9917x+5.7268 = 0$$

solving the quadratic equation by the expression

$$x = \frac{-b-\sqrt{b^2-4ac}}{2a}$$

$$x = \frac{6.9917-\sqrt{48.884-8.934}}{.78}$$

$$= \underline{0.847 \text{ N HF}} \text{ as compared with a value of 0.85 N HF}$$

used to compute the equilibrium constant K.

A similar example for NH_4F plus 2N H_2SO_4 where the average K value is 0.269 and N NH_4F plus 2N H_2SO_4 is 0.77N, would be:

$$K = \frac{x \times x}{(NH_4F-x)(H_2SO_4-x)}$$

$$0.269 = \frac{x^2}{(0.77-x)(2-x)}$$

$$0.269 = \frac{x^2}{1.54-2.77x+x^2}$$

$$0.731x^2+0.745x-0.4143 = 0$$

solving the quadratic equation we obtain for x,

$$x = \frac{-.745+\sqrt{0.5550+1.2114}}{1.462}$$

$$= \frac{0.391 \text{ N HF}}{}, \text{ as compared with a value of } 0.4\text{N HF}$$

used to compute the equilibrium constant K.

The results of these calculations are listed in Table LXXX.

Table LXXX

Comparison of N HF used to calculate average K values with N HF calculated using average K values.

N HF (used to calculate average K value for 4N H_2SO_4)	N HF (calculated using average K value for 4N H_2SO_4)
.35	.359
.75	.748
.85	.847
1.0	1.000
1.15	1.13
1.25	1.22
1.35	1.295
1.5	1.41

N HF (used to calculate average K value for 2N H_2SO_4)	N HF (calculated using average K value for 2N H_2SO_4)
.2	.270
.3	.352
.35	.376
.4	.391
.45	.421
.5	.443
.55	.465

It is noted that where the equilibrium constant K for a specific concentration of N HF was below the average K value, the N HF value calculated using the average K value was generally less than the corresponding N HF value used to calculate the average K value. The reverse is true when the equilibrium constant K for a specific concentration of N HF was above the average K value.

The law of mass action evidently holds within reasonable accuracy when applied to the equation

$$NH_4F + H_2SO_4 \rightleftharpoons (NH_4)HSO_4 + HF \qquad (2)$$

for values of 2N H_2SO_4 and 4N H_2SO_4, plus varying additions of NH_4F, with the exception that the equilibrium constant K varies with the concentration of H_2SO_4 and had to be computed separately for 2N and 4N H_2SO_4.

As a further check on this feature, it was attempted to apply the Law of Mass Action to the reaction when the concentration of NH_4F remained the same and the concentration of H_2SO_4 varied. The concentration of NH_4F was constant at 0.05N, the concentrations of H_2SO_4, 0.5, 1, 2, 4, 6, 8 and 10N, and the equilibrium constants K used were those found previously, 1.39 and 0.216 for NH_4F added to 4N H_2SO_4 and 2N H_2SO_4 respectively. As an example with K = 1.39, and 0.5N H_2SO_4

$$K = \frac{[HF][(NH_4)HSO_4]}{([NH_4F]-[HF])([H_2SO_4]-[(NH_4)HSO_4])}$$

$$1.39 = \frac{x \times x}{(0.05-x)(0.5-x)}$$

$$1.39 = \frac{x^2}{0.025-.55x+x^2}$$

$$0.39x^2-0.7645x+0.03475 = 0$$

solving the quadratic equation we obtain for x,

$$x = \frac{.7645-\sqrt{.5845-.0543}}{.78}$$

$$= 0.047 \text{ N HF}$$

Similar calculations were made using K = 0.269, and the results for both are given in Table LXXXI.

Table LXXXI

Calculated N HF using average K values with a constant concentration of NH_4F plus varying concentrations of H_2SO_4

N NH_4F	N H_2SO_4	K	N HF (calculated)
0.05	0.5	1.39	0.047
0.05	1.0		0.048
0.05	2.0		0.049
0.05	4.0		0.050
0.05	6.0		0.050
0.05	8.0		0.049
0.05	10.0		0.049
0.05	0.5	0.269	0.038
0.05	2		0.046
0.05	4		0.048
0.05	6		0.048
0.05	10		0.049

The results from these calculations are as expected, with the reaction (2) going further to completion as the strength of the H_2SO_4 present in the solution is increased. This is as it should be, for in Figure 3 it is seen the rate of dissolution of the titanium slowly rises as the normality of the H_2SO_4 (with a constant amount of NH_4F added) is increased, and the concentration of HF present also increases. However, a quantitative test showed that there is a difference in the increase of rates.

The rates of dissolution V, of titanium in pure HF was computed using the empirical equation

$$V = 459N^{2/3} \text{ mm}^3/\text{cm}^2\text{-min.}$$

derived by previous investigators [2] for the rate of dissolution of

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2) Straumanis, M. E., and Chen, P. C., op. cit. p. 236

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titanium in HF concentrations between 0.02N and 0.2N.

Substituting, in the the equation just mentioned, the values from Table LXXXI for N of HF obtained from 0.5N H_2SO_4 plus 0.05N NH_4F and 10 N H_2SO_4 plus 0.05N NH_4F, we obtain

$$V_1 = 459 \times 0.047^{2/3} = 59.80 \text{ mm}^3/\text{cm}^2\text{-min.}$$

$$V_2 = 459 \times 0.049^{2/3} = 61.46 \text{ mm}^3/\text{cm}^2\text{-min.}$$

The increase in rates of dissolution of Ti, increasing the concentration of pure HF from 0.047 to 0.049N, is therefore

$$61.46 - 59.80 = 1.66 \text{ mm}^3/\text{cm}^2\text{-min.}$$

The increase in rates of dissolution of Ti arrived at from the experiments using 0.05N NH_4F in the presence of 0.5 and 1ON H_2SO_4 (Tables II and XIV), and where the concentration of HF also increases from 0.047 to 0.049 gives,

$$42.0-29.26=12.74 \text{ mm}^3/\text{cm}^2\text{-min.}$$

Therefore, the rise in rates of dissolution with the same concentrations of HF is larger in the second case than in the first. From this it follows that the H_2SO_4 also contributes to the rate of dissolution, if HF is present, in agreement with former statements. (see page 26, Table VII)

All these results illustrate that the law of mass action holds quite well when applied to the equation

$$NH_4F + H_2SO_4 \rightleftharpoons (NH_4)HSO_4 + HF \quad (2)$$

with the exception that some unknown factor necessitates for best accuracy that the equilibrium constant K be computed separately for each concentration of H_2SO_4.

PART II

Passivation Phenomenon

It was noticed during the investigation of potential measurements and dissolution rates of titanium (Chapter F) that on adding large amounts of ammonium fluoride to a 2N H_2SO_4 electrolyte, a passivation of the titanium took place. This passivation manifested itself in the decrease in rates of dissolution of Ti as follows:

Electrolyte		Rate of Dissolution(mm^3/cm^2-min.)	
2N H_2SO_4	4N NH_4F	560.6	(Table XLVIII)
2N H_2SO_4	5.77N NH_4F	35.	(Table LIV)

The potential of the titanium electrode also became steadily more negative as additional NH_4F was added to the electrolyte: (see Figure 9)

Electrolyte (160c.c.)		Potential (volts H_2 scale)	
2N H_2SO_4	1/20N NH_4F	-.57	(Table XXIX)
2N H_2SO_4	5.77N NH_4F	-.91	(Table LIV)

This fact, that during passivation the potential becomes steadily more negative (as increasing amounts of NH_4F are added) is contrary to all other observations on passivation, and it is generally accepted [4]

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4) Evans, U. R., op. cit. p. 55

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that the potential will rise and become more positive when a reagent added to an electrolyte brings about the passivation of a metal. To

explore this phenomenon a series of additional experiments were made, consisting of potential measurements, conductivity and overvoltage determinations.

Simple, qualitative experiments were made as follows:

First, preliminary tests were made of the potential of Ti in 2N H_2SO_4 electrolyte in a beaker open to air, with NH_4F added to the electrolyte in increasing amounts. The potential of the titanium became steadily more negative as increasing amounts of NH_4F were dissolved in the 2N H_2SO_4. However, after a certain concentration of NH_4F in the 2N H_2SO_4 had been reached, the titanium electrode turned dark, and the hydrogen evolution, which up to this point had been strong, slowed drastically. The potential which had decreased from a value of around -.595 volts to over -.900 volts, rose very quickly to a value of about -.680 volts, then as still further NH_4F was added the potential gradually dropped to -.780 volts and remained constant there. (Table LII, Figure 10) A quite similar occurence took place when the test was repeated with a 2N HF electrolyte instead of the 2N H_2SO_4 electrolyte. (Table LIII, Figure 10)

Quantitative tests were made on the rates of dissolution and potential of the titanium electrode in a nitrogen atmosphere with electrolytes consisting of 140 c.c. of 2N H_2SO_4 plus 30 grams of NH_4F, and 140 c.c. of 1N HF plus 30 grams of NH_4F. This amount of NH_4F was sufficient to reach the concentration where the passivation of the titanium mentioned takes place. The results obtained gave a subdued version of the occurences which happened during the qualitative tests

in a beaker exposed to air. (Figure 11). The maximum negative potentials reached were approximately the same as during the qualitative tests, but the rise in potential afterwards was considerably less. (Tables LIV to LVII). The average maximum rates of dissolution of the Ti were very much less than those of Ti in acid mixtures containing less NH_4F, and also in a N_2 atmosphere.

Electrolyte	Rate of Dissolution(mm^3/cm^2-min.)	
140 c.c. 2N H_2SO_4 30g. NH_4F	27.8	(Table LV)
100 c.c. 2N H_2SO_4 0.5N NH_4F	175.0	(Table XLIII)
140 c.c. 1N HF 30g. NH_4F	24.07	(Table LVI)
100 c.c. 1N HF	588.0	(Figure 6)

After the electrode was taken from the N_2 atmosphere it was still bright and shiny, and there was no dark film on the titanium surface as was formed during the tests made in air. This indicates that the passivation observed is not dependent entirely on the formation of a surface film. However, when the acid film clinging to the titanium surface was washed away with a stream of water, the surface immediately oxidized and turned dark. The oxidized titanium electrode was placed in the same 2N H_2SO_4 and 1N HF electrolytes saturated with NH_4F, as were used during the tests in a N_2 atmosphere, in a beaker open to the air, and potential measurements made. These potential measurements gave the same general pattern as was observed for the first qualitative tests. (see Tables LII, LIII, LVIII, LIX, and Figures 10, 12). With the case of the oxidized titanium electrode the maximum negative potential (-.920 volts average) was obtained

almost immediately as the electrolytes used already contained sufficient NH_4F (30 grams NH_4F in 165 c.c. of acid mixture) to produce the passivation previously mentioned. There was good hydrogen evolution from the oxidized titanium surface until the maximum negative potential was reached. Whereupon the rate of dissolution as before, was cut sharply.

A further test with the titanium electrode in 165 c.c. of an acid mixture containing 30 grams of NH_4F and 1N HF, first in a nitrogen atmosphere then in an oxygen atmosphere, gave no changes in potential measurements with the changes in atmospheres. (Table LX, Figure 13), after the maximum constant negative potential had been reached in a N_2 atmosphere. However, the electrode was dull and oxidized when taken from the acid mixture.

Theory of Local Elements:

In order to explain this passivation phenomenon of the titanium, it is first necessary to describe the theory of the dissolution of titanium by the activity of local cells.

Previous investigators 2)5) have shown that the dissolution of titanium in hydrofluoric acid is likely an electrochemical process,

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2) Straumanis, M. E., and Chen, P. C., op. cit. p. 235

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5) Straumanis, M. E., and Chen, P. C., op. cit. p. 238

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the velocity of which is determined by the activity of local cells. Normally, titanium is covered by a protective film which is porous, so that the metal is partially protected by the film and partially exposed through the pores to the corroding medium. Then when the pores become widened by the hydrofluoric acid dissolving the protective film, still more underlying local cathodes (or cells) are exposed to the acid, and rate of dissolution increases. The cathodes of the local cells are the impurities in the titanium, and the common anode, for all the local cells, is the pure titanium. The film on the metal may act as a cathode only if it has a low electrical resistance and low overvoltage. The potential difference of these local cells E'-N (where E' is the dissolution potential of the titanium itself and N the hydrogen overvoltage of the local cathodes) is small. The resistance r of the acid in the pores might be quite high, so that the current i produced by one of the local cells is

$$i = \frac{E'-N}{r} \qquad (13)$$

and is minute.

When z is the number of local cathodes per unit area, and z' the number of active cathodes in this unit area not shielded by the protective film, the total current produced will then be

$$I = z' \frac{E'-N}{r} \qquad (14)$$

To express this in terms of the rate of dissolution V, it is necessary to add a factor k[14) 15)], then

$$V = k\, z' \frac{E'-N}{r} \qquad (15)$$

14) Straumanis, M. E., Korrosion u. Metallschutz, 9, 1, 29, (1933)

15) Straumanis, M. E., Korrosion u. Metallschutz, 14, 81, (1938)

From this it is seen the important controlling factors of the rate of dissolution are: (i) the electromotive force or potential of the anode, (ii) the resistance of the electrolyte, and (iii) hydrogen overvoltage of the local cathodes. Each of these qualities renders a possible explanation of the passivation of the titanium, and which will be discussed next.

The Mechanism of the Passivation Phenomenon

(i) The first possible explanation for the titanium passivation is that the NH_4F added to the electrolyte may cause some changes in the surface of the titanium during dissolution, which will cause potential changes and lead to a decrease in the rate of dissolution. This possibility was considered by using a model element, Ti-HF-Pt, short circuited through a milliammeter to study the changes of the potential of Ti versus current density. Two different titanium electrodes were used on separate occasions for the Ti electrode in the model element. One of these was of Remington Arms titanium, and the other of purer Battelle Institute titanium, to see if the impurities in the titanium might be exerting some effect on the passivation observed. This was

not the case, and results following the same general trend were obtained with both electrodes. The methods followed in conducting these tests and the results obtained are described in detail in Chapter H.

From these results it can be concluded that the negative potential was most negative (-.914 volts) during the self dissolution of the titanium, when the Pt electrode was not in the circuit. Then when the Pt electrode was in the circuit, the potential increased and was at its least negative value (-0.4 volts). Therefore, the potential of Ti reaches its most negative value when the anodic current passing through the solid/liquid interface approaches zero. Consequently, if the rate of reaction decreases and simultaneously the potential becomes more negative, the latter cannot be responsible for the decrease in rate, and the decrease in rate must be due to some other factor. If this were not so, then the more negative potential should induce a greater rate of dissolution, as shown by the following example:

Taking a hypothetical value for the overvoltage N of -0.3 volts, and substituting in equation (13), we get,

$$i = -0.4-(-0.3) = -\frac{0.1}{r}$$

if the potential of the dissolving metal now becomes more negative

$$i = -0.914-(-0.3) = -\frac{0.614}{r}$$

with $i = \frac{0.614}{r}$ greater than $i = \frac{0.1}{r}$

So, the change in potential in the case of passivation of Ti is not the cause of passivation, but only a consequence of the reduced rate

of dissolution, which decreases because of some other reasons.

(ii) The second possible explanation of the passivation of the titanium might be due to the increased resistance of the acid mixture from NH_4F additions, and the formation of a film of high resistance on the surface of the Ti electrode.

This film formed on the surface of the Ti might possibly be a $[Ti\ F_6]^{---}$ complex formed from the reaction of NH_4F with both $Ti\ F_3$ and $Ti\ F_4$ molecules present in the solution, either together or separately.

$$Ti\ F_3 + 3N\ H_4F \rightarrow (NH_4)_3\ [Ti\ F_6]$$
$$Ti\ F_4 + 2N\ H_4F \rightarrow (NH_4)_2\ [Ti\ F_6]$$

or
$$Ti\ F_3 \rightarrow Ti^{+++} + 3F^-$$
$$Ti^{+++} + 6F^- \rightarrow [Ti\ F_6]^{---} \text{ or } [Ti\ F_6]^{--}$$

These complex salts are soluble in water, but it is possible that in the presence of air some complexes containing oxygen are formed, which are insoluble in acid. This follows from the fact that no such films are formed in an inert nitrogen atmosphere. The formation of such a film on the surface of the titanium would slow dissolution and make the metal passive, as it would cover the local cathodes, smother their action, and not allow further corrosion. However, as the film in this case did not adhere firmly to the titanium, and could be easily removed by washing with a stream of water, it is doubtful if the film had much effect on the rate of dissolution.

An attempt was made to measure the resistance of this surface

film on the titanium electrode, and this procedure is outlined fully in Chapter I.

It was found that the current dropped rapidly to a low, steady value when the Ti electrode was being polarized, showing that the titanium was going passive quickly, and some sort of a protective film forming on the surface. This film only partially slowed the current, for scratching it to expose a fresh surface of titanium caused the current to rise only slightly, then drop again as the film once more covered the freshly exposed surface. This is in agreement with the film only being loosely attached to the surface of the titanium.

Concerning the resistance of the electrolyte, it was found in every case with increasing amounts of NH_4F that the resistance of the solutions decreased when NH_4F was added (Table LXVII). Which dismissed the argument of passivation being due to NH_4F increasing the resistance of the acid mixture.

So, the passivation of titanium in the presence of large amounts of NH_4F may be only partially explained by the formation of surface films on the titanium.

(iii) The third possible explanation for the passivity of titanium may be that the overvoltage N of the local cathodes may rise in the presence of large amounts of NH_4F. To test this possibility, overvoltage measurements were made on platinum and copper electrodes in 56 c.c. of 4N HF plus NH_4F and 56 c.c. of 4N HF plus agar-agar. The procedure followed is described in Chapter J and the results obtained listed in Tables LXIX to LXXVII.

All the measurements made showed definitely that the hydrogen overvoltage of the metals platinum and copper increased with increasing concentrations of NH_4F in the electrolyte. This was characterized by the increase of the constant "a" (Table LXX, Figure 23), while the slope constant "b" was not so strongly affected. Even at low current densities (Figure 24), "a" increased strongly and steadily. The overvoltage then is the only quality which changes with increasing NH_4F in such a manner that it causes a decrease in the rate of dissolution of Ti. In the expression

$$V = k\, z' \frac{E'-N}{r} \qquad (15)$$

if the overvoltage -N is increased, and all the other values remain unchanged (E' may even become more negative), then V will decrease. So it can be concluded that the passivation of titanium in solutions containing large amounts of NH_4F is caused by the increased hydrogen overvoltage of the cathodic impurities on the titanium surface.

This conclusion can be confirmed by overvoltage measurements made for 4N HF solutions with agar-agar additions also decrease the rate of dissolution (Table XXXV) when added to 1N HF in which Ti is dissolving. Figure 25 shows that the overvoltage on platinum and copper is increased with agar-agar additions. The cathodic impurities on the Ti surface absorb the agar-agar molecules and this decreases their active surface. Therefore the current density will increase, and with it the overvoltage -N, which in turn decreases the EMF of the local cells, and according to equation (15), also decreases the rate of dissolution.

So it is possible to explain the different rates of dissolution of titanium observed in different acids, with and without the additions of NH_4F, and the passivation phenomenon described, on the basis of the simple theory of local elements, as described by equation (15).

Chapter V

Summary

The dissolution of titanium in several acids containing ammonium fluoride was studied in this investigation. Qualitative tests made in varying concentrations of several strong and weak acids, HCl, HNO_3, H_2SO_4, $HClO_4$, CH_3COOH, HCOOH and CF_3COOH, showed no attack on titanium by the acids themselves, but a strong attack when ammonium or sodium fluoride was added to the acids.

The law of mass action holds quite well when applied to the equation

$$NH_4F + H_2SO_4 \rightleftharpoons (NH_4)HSO_4 + HF$$

for the formation of HF from NH_4F added to H_2SO_4, with this HF formed dissolving the titanium.

Further quantitative studies were made of the rates of dissolution of titanium in concentrations of H_2SO_4 and HCl from 0.5N to 10N with a constant concentration of 1/20N NH_4F added; of constant concentrations of 2N and 4N H_2SO_4 with the concentration of NH_4F added varying from 0.05N to 1N, and 0.05 to 2N, respectively; and of a constant concentration of 2N HCl with the NH_4F added varying from 0.05N to 1N. The maximum average rates of dissolution increased on a straight line relationship between the rate of dissolution and the normality of the concentration being varied, in all instances. The only exceptions being with concentrations of less than 0.5N NH_4F added to 2N HCl and

4N H_2SO_4, in which cases the relationship was a slightly curved instead of straight line function. The rates of dissolution were much higher for tests made with increasing concentrations of NH_4F in constant concentrations of H_2SO_4 and HCl, than in increasing concentrations of H_2SO_4 and HCl with constant additions of NH_4F. In every instance the rate of dissolution was greater in HCl plus NH_4F than in H_2SO_4 plus NH_4F. Rates of dissolution in 2N H_2SO_4 with increasing concentrations of NH_4F from 1/20N N to 5.77N, gave increases of 32.7 mm^3/cm^2-min. in 2N H_2SO_4 plus 1/20N NH_4F to 560.6 mm^3/cm^2-min. in 2N H_2SO_4 plus 4N NH_4F, then decreased to 35.14 mm^3/cm^2-min. in 2N H_2SO_4 plus 5.77N NH_4F. The rate of dissolution in pure HF increased rapidly with increasing concentrations of HF, on a straight line relationship between the rate of dissolution and Normality of the HF.

It was shown that H_2SO_4 and HCl also contribute to the rate of dissolution if HF is present.

Electrode potentials developed by Ti in 2N H_2SO_4 with increasing concentrations of NH_4F from 1/20N NH_4F to 5.77N NH_4F, and in pure 0.5N to 3N HF were measured. These electrode potentials decreased from -.572 volts (H_2 scale) in 2N H_2SO_4 plus 1/20N NH_4F to -.910 volts in 2N H_2SO_4 plus 5.77N NH_4F. The electrode potential of Ti in pure HF remained constant at -.78 volts, irregardless of HF concentrations.

Metal salts of platinum, gold, copper, nickel, lead, iron and manganese were added to 1N HF during the dissolution of titanium, and only in the case of the platinum addition was there a change in the electrode potential. The potential rising from -.819 volts (H_2 scale)

to -.653 volts.

The rate of dissolution increased considerably when platinum salts were added to the dissolving acid, and decreased when agar-agar was added.

A study was made of the passivation phenomenon noted for the Ti, which manifests itself in that when large amounts of NH_4F were added to the 2N H_2SO_4 solution the rate of dissolution decreased, but the electrode potential of the Ti continued to become more negative. This feature of a dropping electrode potential during passivation is the reverse of that generally observed. The passivation phenomena was shown to be due to increases in the overvoltage of the cathodes of local cells on the titanium surface, when NH_4F is added to the dissolving acid. The activity of these local cathodes governs the rate of dissolution of titanium. The changing of the electrode potential had no effect on passivation, and the formation of a surface film on the titanium only a slight, secondary effect.

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